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Baseline Levels of Platinum and Palladium in Human Tissue

Southwest Research Inst.

Prepared For
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March 1976

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EPA-600/1-76-019
March 1976

PB 251 885

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-600/1-76-019

2.

3. RECIPIENT'S ACCESSION NO.
PB-251 885

4. TITLE AND SUBTITLE
BASELINE LEVELS OF PLATINUM AND PALLADIUM IN HUMAN TISSUE

5. REPORT DATE
March 1976

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
Donald E. Johnson, R. John Prevost, John B. Tillery, David E. Camann and John M. Hosenfeld

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Southwest Research Institute
8500 Culebra Road
San Antonio, Texas 78284

10. PROGRAM ELEMENT NO.
1AA601

11. CONTRACT/GRANT NO.
68-02-1274

12. SPONSORING AGENCY NAME AND ADDRESS
Health Effects Research Laboratory
Office of Research and Development
U.S. Environmental Protection agency
Research Triangle Park, N.C. 27711

13. TYPE OF REPORT AND PERIOD COVERED
Final

14. SPONSORING AGENCY CODE
EPA-ORD

15. SUPPLEMENTARY NOTES

16. ABSTRACT

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Analytical methods are developed for platinum, palladium, and lead using atomic absorption spectrophotometry.

The objective is to determine baseline levels of platinum and palladium in the population and environment prior to wide-spread use of catalyst-equipped vehicles. Lead is determined to ascertain the future epidemiological effect of non-leaded gasoline.

Platinum and palladium concentrations were below the detection limit for Los Angeles, Lancaster, and Sudbury samples. Refinery workers' urine and refinery air samples has detectable concentrations of both metals.

Higher lead values were observed in Los Angeles samples taken near the San Diego Freeway than in samples taken in the high desert area of Lancaster, California.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Platinum Palladium Lead Bioassay Air pollution Water analysis Soil analysis	Catalytic converters		06, F

PRICES SUBJECT TO CHANGE

18. DISTRIBUTION STATEMENT
RELEASE TO PUBLIC

19. SECURITY CLASS *(This Report)*
UNCLASSIFIED

20. SECURITY CLASS *(This page)*
UNCLASSIFIED

21. NO. OF PAGES
252

22. PRICE
9.00-2.25

EPA Form 2220-1 (9-73)

EPA-600/1-76-019
March 1976

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HEALTH EFFECTS RESEARCH LABORATORY
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This report was submitted in fulfillment of Project No. 01-3881-003 and Contract No. 68-02-1274 by Southwest Research Institute under the sponsorship of the Environmental Protection Agency. Work was completed as of August, 1975.

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ACKNOWLEDGMENTS

The work accomplished in this study was materially assisted by the interest, experience, and unstinting cooperation of personnel of the Catalyst Research Program, EPA, Research Triangle Park, and particularly that of Mr. John Moran, Dr. Robert Bruce, Ms. Vandy Duffield, and Dr. Doug Worf of that facility. The thanks of our entire study team is offered to these individuals for the help they provided. This study was performed on locations in California, Pennsylvania, New Jersey, Ontario and Texas; without the significant cooperative efforts of a large number of diverse organizations at these locations, accomplishment of the study objectives would have not been possible. Organizations to which particular acknowledgment is due include:

The School of Public Health and
The Office of Married Student Housing
UCLA

Mira Loma Hospital
Lancaster, California

Wadsworth Veterans Administration Hospital
Los Angeles, California

Internation Nickel Company
New York, New York - Toronto, Ontario -
Copper Cliff, Ontario

Matthey Bishop, Inc.
Malvern, Pennsylvania & Winslow, New Jersey

Because epidemiological studies of this nature cannot be performed without the cooperation and aid of individual volunteers who give of their time and efforts and, literally, blood, the authors wish to extend their personal thanks to the participants in California, Ontario, and New Jersey who made this study possible.

I. CONCLUSIONS

1) Baseline levels of platinum and palladium in the environment (ambient air, surface soil and tap water) and in urban populations (children, young adults, elderly - male and female - blood, urine, hair, feces and autopsy samples - liver, kidney, spleen, muscle and fat) of Southern California (Los Angeles and Lancaster) are extremely low. The levels in nearly all samples were below the detectable limits of the analytical methods. These samples were collected in September 1974 prior to the introduction of the 1975 automobiles which were equipped for the first time with the catalytic muffler.

2) The design of the environmental epidemiology study of baseline levels of platinum and palladium was such that, if needed, a future survey could be conducted to determine whether or not the operation of the catalyst-equipped vehicles has altered these baseline levels.

3) The levels of lead in ambient air and surface soil were substantially higher in the study areas of Los Angeles than in Lancaster. There were no differences in lead content of tap water collected from residences in these study areas. Examination of exterior paint on the surfaces of residences in Los Angeles indicated a low level of lead.

4) Lead in blood, urine, long hair and short hair was significantly higher in study participants in Los Angeles than in those

in Lancaster. Feces lead (a good indicator of orally ingested lead) was slightly higher in Lancaster residents than those studied in Los Angeles. The residents studied in Los Angeles were selected from those living very close (within two blocks) and on the downwind side (prevailing winds) of a major expressway (approximately 225,000 cars/day. Surface soil lead values showed very high levels close to the freeway with decreasing values with distance away from the expressway. Thus, given the known high lead values in air and soil from the expressway source and the elimination of the other common sources of lead ingestion (food, water, paint), it appears highly likely that automotive lead emissions were responsible for the observed lead levels in blood, hair and urine of the Los Angeles study participants.

5) The examination of ambient air and miners for levels of platinum and palladium in the Sudbury area of Canada did not provide definitive data on the relationship of ambient air levels of platinum and palladium. This was because air levels (except for one part of the plant) were below detectable levels.

6) Data from platinum and palladium refineries indicate that measureable levels of platinum (0.5-2.6 μg/liter) and palladium (0.3-6.3 μg/liter) are found in urine of workers exposed to air containing 0.02-0.2 μg/m^3 platinum and .001-0.36 μg/m^3 of palladium. Measureable levels were not found in blood from these workers.

7) The information from the refineries indicates that it is likely that measureable levels of platinum and palladium would be seen in the general population when ambient levels of these two metals approach 0.1 $\mu g/m^3$. The metals would appear initially in urine rather than blood. The data do not provide any inferences with regard to the absorption of soluble or insoluble forms of the metals. It is probable that metal particles emitted from the catalytic muffler would have to be in the respirable range for inhalation and absorption. Reports from Dr. Moore (EPA, Cincinnati) indicated that both soluble and insoluble forms of respirable platinum and palladium were absorbed in animal experiments.

II. RECOMMENDATIONS

1) The original plan was to examine blood, urine, hair and feces in refinery workers and to collect autopsy samples from former refinery employees. The refineries agreed to blood and urine collections only. Arrangements to collect autopsy samples from pathologists in the area of the refinery were unsuccessful. Additional data are needed on the distribution of platinum and palladium in human tissue other than blood and urine following exposure to air containing the two metals at the 0.01-0.1 $\mu g/m^3$ levels. It is likely that autopsy samples could be collected if additional effort were expended and if the sampling period covered at least two years.

2) Additional data to define the relationships between air levels of platinum and palladium, and tissue levels in the general population (different age groups, both sexes) are needed, but it is recommended that the collection of these data be deferred until there is more information available on quantities and types (respirable-nonrespirable, solubility, chemical form) of the two metals emitted from the catalytic mufflers. Data are available which indicate that particles of these two metals are emitted, but the physical and chemical characteristics of these particles have not yet been established.

3) It appears that the placement of priorities for evaluation of the potential health effects of the catalytic mufflers should emphasize the production of sulfuric acid and sulfates. Additional effort should

the production of sulfuric acid and sulfates. Additional effort should be directed at characterizing the emissions from these muffler systems. It is strongly recommended that research be initiated to evaluate the health impact of the catalytic muffler on populations living in the immediate vicinity of major expressways with regard to evaluated levels of sulfuric acid and sulfates from automotive emissions. It is recognized that the muffler has been in use for only one year on new automobiles (1975), so the impact will not be significant for perhaps one or two more years, but efforts need to be initiated so that the necessary techniques for ambient air measurements and measurement of proper health effects indices can be perfected.

III. INTRODUCTION

Catalytic converters were introduced (late September 1974) on many of the 1975 model automobiles in the United States to reduce emissions of carbon monoxide and unburned hydrocarbons. The catalysts used small quantities of platinum and palladium, and there have been some indications of emissions of particles of these metals. Health effects fron exposure to platinum and palladium reviewed in a previous part of this study (1) indicated that soluble forms of platinum can create allergic responses in sensitive individuals. However, little information is available concerning long-term chronic exposure of humans to low levels of platinum or palladium, in particular for groups that may be at greater risk such as the young or aged and for individuals with some type of medical impairment. There are also some indications that platinum can be methylated, thus possibly producing a more toxic component.

The EPA has placed additional emphasis on the collection of biological data on platinum (Pt) and palladium (Pd); since there is limited biological experience with them, they are likely to be persistent, they may be metabolized to more toxic products, and exposures will involve the general population. Emissions from vehicles equipped with the oxidation catalysts contain components other than Pt and Pd which may create health effects. The production of sulfates and sulfuric acid by the catalyst is particularly important. This project has been directed at the possible introduction of Pt and Pd as particulates and with the reduction of lead emissions to the environment, as the catalyst equipped vehicles require non-leaded gasoline.

Several papers were presented at a symposium, entitled "Health Consequences of Environmental Controls: Impact of Mobile Emissions Controls", relative to the problems of trace metals involved in the usage of the oxidative catalyst equipped vehicles. The subjects of these papers included examination of emission data, toxicological investigations of the two metals, development of analytical assay methods, review of relevant health effects information, effects of the usage of the catalyst on world markets of Pt and Pd and the design of an environmental epidemiology study to collect health effects data on Pt and Pd. Many of the papers discussed plans for conduct of their studies. The overall intent of the symposium was to review the available data and to make recommendations as to the additional information needed to make decisions regarding the safety of the catalytic muffler. Specifically, these investigations were to provide data to assist both EPA and affected industries in solutions to this and future problems which impact on public health.

The design of this program was presented at this symposium;[(1)] thus, its contents were reviewed by academic, government, nonprofit and industrial organizations. The project has included two types of environmental epidemiology studies: one directed at determining baseline levels of platinum, palladium, and lead in the general population prior to the introduction of the catalysts equipped vehicles, and the second aimed at determining platinum and palladium residues in occupationally exposed individuals with the intent to define the relationship between airborne levels and tissue levels of the two metals.

The baseline study was to be conducted in Southern California with the selection of a population with relatively heavy exposure to automobile emissions and also in a second population with low exposure to vehicular emissions. Three age groups of both sexes were to be examined; children, young adults and elderly. The demographic make-ups of the two populations were to be as similar as possible. Tissue samples were also to be collected at autopsy from individuals from the study area to determine levels of the three metals in different tissues.

The location of the survey of a population with high exposure to vehicular emissions was selected so that it would be able to utilize ambient air data from the L.A.C.S. located along the San Diego Freeway in Los Angeles. The design of this baseline study was such that it would provide an accurate estimation of levels of Pt, Pd and lead just prior to the introduction of the catalytic mufflers. These data could then be used for comparison with similarly collected data for subsequent years, assuming continued usage of the catalyst. The baseline data would serve a very useful purpose for determining the impact of this new technology on the environment and on tissue levels.

The occupationally exposed populations were to be drawn from platinum and palladium refineries located in New Jersey and from the mining and processing of ore containing Pt and Pd located in the

Sudbury, Canada area. The reasons for including mining and refinery workers is that the mining was likely to involve exposure to insoluble forms of the two metals, while the refineries will involve at least a portion of the metals in the soluble form. These surveys were also to include examination of autopsy tissue from deceased employees at these sites.

IV. EXPERIMENTAL

A. Selection of Study Sites

1. Baseline

The Los Angeles area was selected for the high exposure to vehicular emissions because it has a very large population and a high percentage of new automobiles projected for the new car year (1975) equipped with the catalyst, emissions from heavy industry can be minimized by selection of areas within the city, and the EPA study (LACS) was located in the area. After an on-site inspection of the area, it was decided to conduct the study on the east side of the San Diego Freeway (within 2 blocks) bounded on the north by Sunset Boulevard and on the south by National Boulevard. The San Diego Freeway has a traffic density of 225,000 - 250,000 cars per day in this area. The prevailing winds in this area are from the west and southwest; thus, the study area is downwind of the freeway much of the time. Much of the residential area within the above boundaries was at the same level as the freeway, and the residents were primarily middle class residing in single and multiple dwellings.

The low exposure area selected for the baseline study was in Lancaster, California. This city is located 70 miles northeast of Los Angeles in the high desert. The city is not affected by smog from the Los Angeles basin. The city has a population of 30,948 and has light industry with no known point sources of lead, platinum or palladium. The surrounding area is very sparsely inhabited. The population from this area was drawn from various areas of the city with the predominate workplace (of those studied) being a county hospital located in the fringe of the city.

2. Mining

There are only very small quantities of Pt and Pd mined in the United States, principally as a residue of other metal mining. The Sudbury area of Canada is the largest producer of these two metals in North America. The ore in this area contains very low levels of Pt and Pd as compared with South African ore which is 10-20 times higher. The primary metals produced in Sudbury are copper and nickel, with smaller quantities of iron. Gold, silver, tellurium, osmium, rhodium, selenium, cobalt, platinum and palladium are produced from the ore residue. Platinum and palladium are processed to a concentrate and then sent to refineries for further processing.

The largest mining company in the Sudbury area is the International Nickel and Copper Ontario (INCO). Contacts were made with this company through offices in New York and Toronto. This organization gave their approval for the conduct of the survey at their plant in Sudbury contingent upon approval of the unions prior to contacts with union employees. INCO was very cooperative and provided considerable assistance in the conduct of the survey at their plant.

3. Refineries

There are two primary platinum and palladium refineries located in the United States. Each of these companies was approached for their cooperation and participation in the study. Both companies had considerable reservations about the study. After numerous discussions, each agreed to participate for a portion of the planned survey. Both of the refineries studied are located in New Jersey.

One of the companies agreed to collect samples of blood and urine from employees within the refinery and to collect air particulate samples within the work environment of these employees. The company performed analysis on the collected samples for platinum and palladium and submitted the results to SwRI.

The second company (Matthey Bishop, Inc., Malvern, Pa.) collected blood and urine samples from their refinery employees, along with pertinent information on each employee sampled such as age, sex, length of time with company, duties within plant, smoking history, and ethnic origin. The company also collected air particulate samples in the plant during the week that the employees were sampled. All collected samples were divided, with a portion to the company laboratories and the balance to SwRI.

B. Recruitment of Study Participants

1. General Approach

The general approach taken in this study to solicit and recruit volunteer participants has been to work through organizations.

The organizations worked with directly have been employers of volunteer participants and a university attended by other volunteer participants.

Another method used successfully by this study team utilizes house-to-house surveys to recruit volunteer participants. House-to-house surveys were considered and ruled out as unnecessary in this study due to the degree of precision needed in positioning of the place of residence of the volunteers. In this study, it is sufficient that the volunteers live within a specific region or work for a specific employer. The precision required for this study can be well achieved by working through organizations. Working through organizations provided the study team with a number of advantages over house-to-house surveys. Principal personnel in the organizations served as points of initial contact, liaison during planning recruitment activities, and provided aid during recruitment, selection, and sample gathering activities. Volunteers feel more comfortable in familiar surroundings during recruitment and sample gathering activities.

The first step taken in the recruitment activities, when working through organizations, is initial telephone contact with a potential participant organization. In many cases, preliminary telephone calls are required to appropriate state, federal, or local government agencies or to local universities and industries to determine the background of circumstances in the particular area which might affect successful recruitment and use of human volunteers. In this study, preliminary phone calls were made to each of the types of institutions listed above.

The initial telephone contact is used to briefly describe the study and the need for human volunteers. A minimum of information regarding the study is provided at this point, as the primary goal of the initial phone call (or calls, as usually occurs) is to establish a person in the organization who will serve as the initial contact and to establish a time and place for meeting in person with representatives of the organizations to discuss in detail the specific proposal of study. Arrangements are usually made at this point to forward to the initial contact person a set of written materials explaining in detail the background of the study and the specific requirements needed from the participating organization. These are forwarded for review before the initial meeting in order that the potential participating organization can better prepare for the meeting.

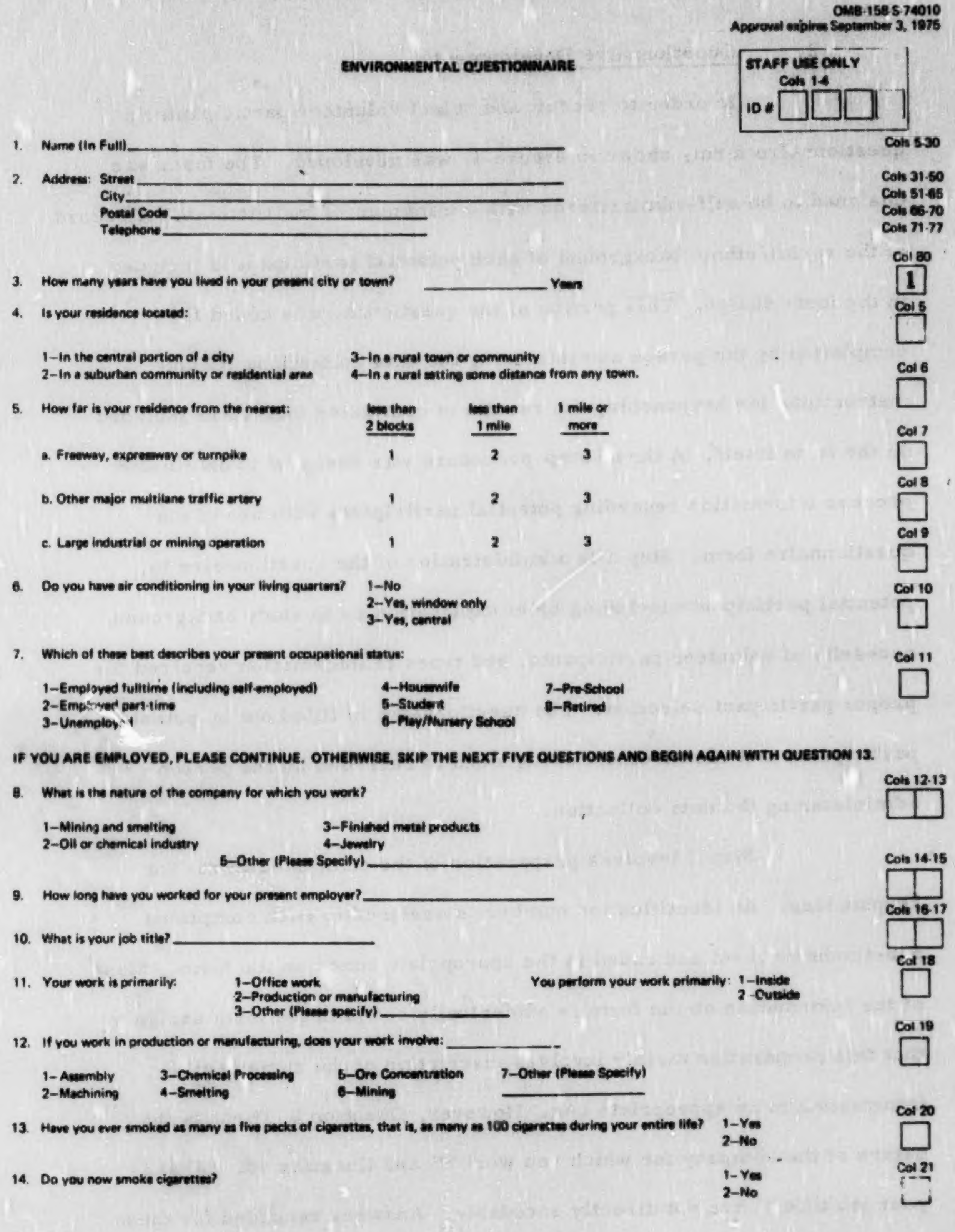
At the initial meeting, the potential organization is briefed regarding study requirements. The principal objective of the meeting is to obtain permission for performing the study. Other objectives include establishment of a principal person for contact, a time and place for meeting with potential volunteers, and establishments of the methods to be used in recruitment acitivities. The initial meeting is followed by advertisement of the study which specifies the place and time for the meeting with potential volunteers, and, finally, the recruitment meeting where materials explaining the purpose and requirements of the study are provided and questionnaire forms are completed by volunteers.

2. Questionnaire Development

In order to recruit and select volunteer participants, a questionnaire form, shown in Figure 1, was developed. The form was designed to be self-administered with a minimum of instructions. A record of the racial/ethnic background of each potential participant is included in the form design. This portion of the questionnaire is coded for completion by the person administering the data collection. Coded instructions for keypunching the results of completed forms are included on the form itself. A three-step procedure was designed to obtain and process information regarding potential participants with use of the questionnaire form. Step 1 is administration of the questionnaire to potential participants including brief explanation as to study background, necessity of volunteer participants, and types of information required for proper participant selection. The questionnaire is filled out by potential participants and racial/ethnic background is recorded by the person administering the data collection.

Step 2 involves preparation of the completed forms for keypunching. An identification number is assigned to each completed questionnaire form and coded in the appropriate boxes on the form. Most of the information on the form is numerically coded in the form design so that this preparation mainly involves inscription of the numerical information in an appropriate box. However, Question 8 "What is the nature of the company for which you work?" and Question 10, "What is your job title?" are not directly encodable. Answers recorded for these

Figure 1. Platinum, Palladium and Lead Questionnaire



OMB-158-S-74010
Approval expires September 3, 1975

STAFF USE ONLY
Cols 1-4
ID # ☐☐☐☐

ENVIRONMENTAL QUESTIONNAIRE

1. Name (In Full)______________________________ Cols 5-30

2. Address: Street______________________________ Cols 31-50
City______________________________ Cols 51-65
Postal Code____________________ Cols 66-70
Telephone____________________ Cols 71-77

Col 80 1

3. How many years have you lived in your present city or town? __________ Years

4. Is your residence located: Col 5 ☐

1–In the central portion of a city
2–In a suburban community or residential area
3–In a rural town or community
4–In a rural setting some distance from any town.

5. How far is your residence from the nearest:

	less than 2 blocks	less than 1 mile	1 mile or more	
a. Freeway, expressway or turnpike	1	2	3	Col 6 ☐
b. Other major multilane traffic artery	1	2	3	Col 7 ☐
c. Large industrial or mining operation	1	2	3	Col 8 ☐

6. Do you have air conditioning in your living quarters? Col 9 ☐
1–No
2–Yes, window only
3–Yes, central

7. Which of these best describes your present occupational status: Col 10 ☐

1–Employed fulltime (including self-employed)
2–Employed part-time
3–Unemployed
4–Housewife
5–Student
6–Play/Nursery School
7–Pre-School
8–Retired

Col 11 ☐

IF YOU ARE EMPLOYED, PLEASE CONTINUE. OTHERWISE, SKIP THE NEXT FIVE QUESTIONS AND BEGIN AGAIN WITH QUESTION 13.

8. What is the nature of the company for which you work? Cols 12-13 ☐☐

1–Mining and smelting
2–Oil or chemical industry
3–Finished metal products
4–Jewelry
5–Other (Please Specify)____________________

9. How long have you worked for your present employer?____________________ Cols 14-15 ☐☐

10. What is your job title?____________________ Cols 16-17 ☐☐

11. Your work is primarily: Col 18 ☐
1–Office work
2–Production or manufacturing
3–Other (Please specify)____________________

You perform your work primarily:
1–Inside
2–Outside

Col 19 ☐

12. If you work in production or manufacturing, does your work involve: __________

1–Assembly
2–Machining
3–Chemical Processing
4–Smelting
5–Ore Concentration
6–Mining
7–Other (Please Specify)
____

13. Have you ever smoked as many as five packs of cigarettes, that is, as many as 100 cigarettes during your entire life? Col 20 ☐
1–Yes
2–No

14. Do you now smoke cigarettes? Col 21 ☐
1–Yes
2–No

Figure 1 (continuation) Platinum, Palladium and Lead Questionnaire

15. If you are a current or an ex cigarette smoker:

Col 22 ☐

a. How many cigarettes do (did) you smoke per day

1–Less than 1/2 pack per day (1-5 cigarettes per day)
2–About 1/2 pack per day (6-14 cigarettes per day)
3–About 1 pack per day (15-25 cigarettes per day)
4–About 1-1/2 packs per day (26-34) cigarettes per day)
5–About 2 packs per day (35 or more cigarettes per day)

b. How old were you when you first started smoking?__________Years

Cols 23 24 ☐☐

c. How old were you when you last gave up smoking, if you no longer smoke?__________Years

Cols 25 26 ☐☐

16. What is your marital status?

1–Single
2–Married
3–Separated
4–Divorced
5–Widowed

Col 27 ☐

17. How many times have you and your family changed living quarters during the last five years?

0–None
1–One time
2–Two times
3–Three times
4–Four times
5–Five times or more

Col 28 ☐

18. What educational level has been completed by the head of your household:

1–Less than 8th grade
2–8th grade
3–High School–Incomplete
4–High School–Completed
5–College–Incomplete
6–College–Completed
7–Graduate School

Col 29 ☐

19. What was your age in years on your last birthday?__________Years

Cols 30 31 ☐☐

20. What is the natural color of your hair?

1–Brown
2–Black
3–Red
4–Blond
5–Gray

Col 32 ☐

21. What is your sex? 1–Male 2–Female

Col 33 ☐

22. Females Only:

Col 34 ☐

a. What is your hormonal status?

1–Pre-puberty
2–Menstrual
3–Menopause

b. Do you use oral contraceptives?

1–Yes
2–No

Col 35 ☐

23. Have you ever experienced any of the lung related problems listed here:

0–None
1–Asthma
2–Emphysema
3–Tuberculosis
4–Histoplasmosis
5–Bronchiectasis
6–Bronchiolitis
7–Bronchitis
8–Tumor or Cancer
9–Other (Please Specify)
____
____

Col 36 ☐

24. Are you presently being treated for any of the illnesses listed here:

0–None
1–Diabetes
2–Thyroid
3–Sickle-cell
4–Kidney disease (Please Specify)
____

Col 37 ☐

25. Are you presently taking prescription medication on a regular, daily basis?

0–None
1–Tranquilizer
2–Stimulant
3–Pain Suppressant
4–Cortisone Type
5–Other (Please Specify)
____

Col 38 ☐

YOU HAVE COMPLETED THE QUESTIONNAIRE
THANK YOU FOR YOUR COOPERATION

STAFF USE ONLY
IMNOWO 1 2 3 4 5 6

Col 39 ☐

Col 80 2

questions have been reduced to the numerical codes shown in Table 1 and encoded in the appropriate boxes on the forms. The third and final step in preparation and processing of the questionnaire data is keypunching the data onto two keypunch cards. Card 1 contains name, address, and telephone number, and card 2 contains covariate data used to select participants and, ultimately, to correlate with the results of analysis of the samples obtained from human volunteers.

3. Backup Materials

A set of backup materials was developed for use in recruiting organizations and in recruiting volunteer participants at each organization. The materials included a narrative summary describing the study and requirements of participating organizations and volunteer participants, a one-page summary of sample collection criteria and procedures for each of the four distinct areas in which organizations and participants were recruited, and a one-page summary of study background and specific requirements for voluntoer participants for each separate organization from which volunteers were obtained. In addition, a one-page brief summary of requirements for autopsy samples in the two areas of Southern California was generated for use in soliciting help in the matter of collecting and providing to this study such samples by appropriate agencies.

Table 1
Numerical Coding of Responses to Questions 8 and 10

Question 8: Code 1 - 4 as indicated on form.
Code 5 in following manner:

5	other, (inappropriately answered)
6	medicine (dentistry)
7	public assistance (fire, police, ambulance)
8	law
9	education
10	business (commercial activity)
11	industry
12	recreation
13	media
14	government (civil service, military)
15	construction
16	research

Question 10: Job Title

0	(inappropriately answered)
1	professional
2	administrative
3	technical
4	clerical (secretary, file clerk, cashier)
5	sales
6	foreman and craftsmen
7	laborer (kitchen, custodial, maintenance, news carrier)
8	assistant (attendant)
9	volunteer worker
10	waiter, waitress
11	teacher
12	librarian
13	heavy motorized equipment operator
14	mining
15	refining
16	electrowinning

4. Recruitment Activities

a. Southern California

The study design incorporated use of volunteer participants living near a freeway in Los Angeles and a second set of volunteer participants living in an area with less exposure to automotive emissions near the Los Angeles area. The design was to match the socioeconomic characteristics of the more and less exposed groups as much as is practical and reasonable so as to minimize spurious effects due to socioeconomic parameters. A number of public organizations in the Los Angeles region were contacted to obtain advice regarding specific areas appropriate for the study design. Principal organizations and persons contacted are the following:

Person	Organization
Dr. Fred Ottoboni Dr. Norm Perkins	State Dept. of Health Berkeley, Calif
Jim Heacock	State Dept. of Health L.A. Branch Office Occupational Health Unit
Dr. Oscar Balchum	USC Medical School Dept. of Chest Medicine
Jack Rogers	L.A. County Dept. of Health Occupational & Radiological Health
Dallas Candy	Acting L.A. County Health Officer L.A. County Dept. of Health
Dr. Stanley Rocow	L. A. County Lung Association
Dr. Thomas T. Noguchi, Medical Examiner	Los Angeles County

Person	Organization
Don Madden	Public Info. Assistant Air Pollution Control District Los Angeles, Calif.
J. A. Stuart, County Air Pollution Control Officer	District 7 California Highway Dept. Los Angeles, Calif.
Howard Lange	Dept. of Health Riverside County
Dr. Ray Thompson	U. C. Riverside
Wesley Sholts, Dir.	Mira Loma Hospital
Ron Huber, Asst. Dir.	L. A. County Health
Dr. Picken, Staff Phys.	
Robert M. Young, Personnel Officer	
Dr. Wright, Chief of Staff	Wadsworth VA Hospital Los Angeles, Calif.
Henry Ford, Office of Director	
Dr. Fishken, Chief of Clinical Lab. Sciences	
Cordell R. Welcome, Office of the Director	
John Valance, Director of Brentwood	
Dr. Jeremiah Thompson, Pharmacology Dept.	UCLA
Dr. David Porter, Pathology Dept.	
Dr. Jane L. Valentine, School of Public Health	
Dr. John F. Schacher, Professor of Infectious & Tropical Diseases, Div. of Epidemiology, School of Public Health (also chairman of human subjects)	

Areas along the San Bernadino Freeway in the vicinity of Pomona, San Bernadino and Riverside and areas along the San Diego Freeway in Los Angeles and in the vicinity of Santa Monica were found to be the best candidates for the study sites with higher exposure. Recruitment through churches, apartment complexes, hospitals, and universities was considered. An area in Los Angeles along the San Diego Freeway in the vicinity of Santa Monica was ultimately chosen for the higher exposure site. The specific area lies immediately west of the San Diego Freeway, in Los Angeles, between National Boulevard and Sunset Boulevard.

Selection of this site was principally for the following four reasons: 1) EPA operates an air monitoring station in the vicinity of the site chosen which is planned for long-term monitoring of the San Diego Freeway. 2) The prevailing wind is from the direction of the ocean, four or five miles away to the west, with little or no industry between the freeway and the ocean. Therefore, heavy metal pollutants found in the air can be related to automotive traffic. This condition is not true for the second major area considered for study, the San Bernadino Freeway. Pollutant levels are generally higher on the San Bernadino Freeway, but some of the pollutants result from industrial, rather than automotive, sources. 3) A UCLA student residential area is located immediately adjacent to the San Diego Freeway, downwind, and UCLA provided approval for volunteer student participation. 4) A large VA hospital, the Wadsworth Veterans Administration Hospital, is located near the freeway with a staff of several thousand, some of whom reside in the primary area of study, downwind of the vicinity of the freeway. Conversations with VA hospital staff indicated necessary cooperation could be expected to recruit volunteer participants among hospital staff and staff families.

Conversations with L.A. County Department of Health officials yielded consideration of a remote county hospital in Lancaster, California, as the best candidate for volunteers from a less exposed area. The area is in Los Angeles County, approximately 40 miles north of Los Angeles metropolitan area, 70 miles out of downtown Los Angeles. The population makeup of the area of Lancaster was estimated to be similar to that found in Los Angeles regarding socioeconomic parameters. Subsequent conversations with administrative staff at the hospital, Mira Loma Hospital, Lancaster, California, indicated that the necessary cooperation could be expected to enable SwRI to recruit volunteer participants among hospital staff and staff families.

Preliminary meetings were held with staffs at UCLA, the Wadsworth Veterans Administration Hospital, and the Mira Loma Hospital. A person responsible for contact was established at each of the organizations:

UCLA	-	Dr. Jane L. Valentine
Wadsworth	-	Cordell R. Welcome
Mira Loma	-	Robert M. Young

For each organization, a specific date, time, and place was established for meeting with potential volunteers, and the meeting was advertised. At UCLA, an article was written and submitted to a campus newspaper, and notices were posted at appropriate bulletin boards in the residential area, a married student housing area where students and student families were located. Some notes were provided directly to residents of the campus housing selected for study. On the appointed day, a meeting was held with prospective volunteers to obtain completed questionnaire forms from all volunteers, both students and student families.

At Wadsworth, an article was placed in the hospital newsletter, and advertisements were posted on appropriate bulletin boards advertising the recruitment meeting. Prospective volunteers completed questionnaire forms and turned them in to the survey team.

At Mira Loma, the recruitment meeting was advertised by placement of notices on appropriate bulletin boards. On the appointed day, SwRI staff first met with principal members of the hospital administrative and medical staff. A certain number of the supervisors then briefed their people regarding the study requirements for volunteers. A subsequent meeting with prospective volunteers was held to obtain completed questionnaire forms from all who volunteered for the study.

The final set of completed questionnaire forms were then prepared for keypunch and the results were sorted and listed for use in selecting specific volunteers. Volunteers selected from the UCLA married student housing area tended to be children and young adults, with some older people. Volunteers selected from Wadsworth tended to be middle and older aged adults, with some younger adults. Volunteers selected from Mira

Loma staff and families were from all three age groups: children, young adults, and older adults.

b. Ontario

The study design incorporated use of volunteer participants occupationally exposed to platinum or palladium. Persons in the mining of precious metal refining industries were considered as the primary candidates to fulfill this study requirement. To the purpose of securing cooperation and participation in the study, the following representatives of International Nickel Company were contacted in New York, Toronto, and Copper Cliff, Ontario:

Person	Organization	Location
J. C. Parlee, Vice Chairman of the Board	INCO	New York
Louis S. Renzoni, Vice President Operations	INCO of Canada	Toronto
Norman Hillier, Mgr. Safety & Plant Protection	INCO, Ontario Div.	Copper Cliff
Hank Derks, Safety & Plant Protection	INCO, Ontario Div.	Copper Cliff
Keith Segsworth, Air Management	INCO, Ontario Div.	Copper Cliff
Bill Brown, Assistant Mgr.	INCO Copper Refinery	Copper Cliff
Pat Scott, Employee Relations	INCO South Mine	Copper Cliff

The offices in Toronto and Copper Cliff were visited to brief appropriate officials regarding the proposed study and to determine an appropriate site for study, if INCO should choose to participate. INCO officials chose to participate in the study and selected a portion of the Copper Cliff which deals with precious metals and a mine area where catalytic converters employing platinum and palladium are used to a great extent.

Questionnaire forms were left with the assistant manager of the Copper Refinery and with the employee relations department at the South Mine at Copper Cliff. Volunteers were recruited by company officials, and forms were completed and returned to SwRI personnel at an appointed date. All volunteers meeting the study requirements of working in an area with exposure to platinum or palladium were selected as participants.

The cooperation and aid supplied to this study by INCO should be especially noted. This company provided in excess of two man weeks of senior level people, free of charge, to aid the initiation of study activities and followed this up by arranging for a barber, two laboratory technicians, and performing air samplings at a number of stations, again without compensation. INCO is due our sincere thanks and compliments and that of the Environmental Protection Agency.

c. New Jersey

Two companies dealing in precious metals refining in New Jersey were selected for study. Persons working in precious metals refining processes where some potential of exposure to platinum or palladium exists were sought as study participants. Officials of each of the two firms were met with to secure cooperation and participation in the study.

One of the firms conducted a study in their refinery and reported the results to Southwest Research Institute.

Matthey Bishop, Inc. collected environmental and human samples at their refinery located in Winslow, New Jersey. These samples were analyzed at Southwest Research Institute. The primary individuals involved with the study at Matthey Bishop were: Mr. V. W. Makin, President and Mr. Orin G. DeLa , Manager of Industrial Relations.

5. Participant Selection

a. Selection Criteria

For each of the four areas studied, distinct selection criteria were developed for recruiting and selecting volunteer participants. In general, the selection criteria can be described with two categories: 1) non-occupationally exposed participants and, 2) occupationally exposed participants.

Selection criteria for the two groups of non-occupationally exposed participants are principally involved with location of residence, age, and sex of the participant. For participants from the area of high exposure near the San Diego Freeway in Los Angeles, the selection criteria included four parameters: 1) normal occupation away from high potential of exposure to lead and precious metals, 2) location of residence, 3) age, and 4) sex. All persons selected as participants lived in the vicinity of the San Diego Freeway downwind of the prevailing wind pattern (east of the freeway). The objective was to recruit three separate age groups with equal numbers of males and females in each age group. The age groups are: 1-16 years, 17-34 years, and 35 years and over (Groups I, II, and III, respectively).

For the second group of non-occupationally exposed participants, those from the area of lower exposure in the vicinity of Lancaster, California, the selection criteria included the same four parameters as for the higher exposed group. However, the residence requirement was much less strict than that for the higher exposed group. It was sufficient that potential participants reside in the general area of Lancaster or Palmdale and that they had no occupation which normally took them into Los Angeles.

The selection criteria for the occupationally exposed participants were limited to two principal requirements: 1) occupation in a job which potentially exposed the participant to significant levels of platinum and/or palladium, and 2) a minimum of six months at the particular occupation. Information regarding age and sex of the participants was obtained, but no specific requirement was enforced regarding these parameters. Using the occupation criteria, participants were recruited in Ontario, Canada in the precious metals mining and refining industry and in New Jersey in the precious metals refining industry.

For each participant, a complete questionnaire form was obtained with the exception of the refiners in New Jersey where only a part of the questionnaire form was used: questions 1, 9, 10, 14, 19, and 21 as presented in Figure 1. In addition to the principal parameters used as selction criteria, data regarding a number of supplementary parameters were also obtained in order to identify certain important socioeconomic and health related data for each individual. These data can be used to establish the gross characteristics of the participants when statistical data are being used in comparisons between different groups of participants. Most important among the supplementary parameters are: years of residence in the city, frequency of change of living quarters, education level of the head of household, and smoking history.

6. Description of Study Participants.

A total of 141 participants were recruited and selected in Los Angeles, 142 in Lancaster, California, and 49 in Ontario through use of the recruitment methods documented here. An additional 61 volunteer participants were obtained in New Jersey by recruitment by company officials in the particular organization chosen for study. For the New Jersey participants, information regarding age, occupation, sex, and smoking history was collected with the partial questionnaire form. The ethnic composition of these 393 volunteer participants is as follows: Los Angeles: 60% white, 40% non-white; Lancaster: 80% white, 20% non-white; Ontario: 100% white; New Jersey: 90% white, 10% non-white.

Pertinent socioeconomic and demographic characteristics for the volunteer participants used in this study are presented in Table 2 and shown in Figure 2. Analysis of the occupations of the participants is provided in Table 3. Separate information is provided for the non-occupationally and the occupationally exposed groups. A complete listing of information on all participants from Los Angeles and Lancaster is given in Appendix A. To utilize the coded information, refer to Figure 1.

C. Collection of Samples

1. Environment

a. Baseline

The baseline study for environmental characterization of platinum, palladium and lead in air, water and soil was performed in Lancaster and Los Angeles. In Los Angeles, the reference point for sample collection was the San Diego Freeway and the sites designated as "A, B, C, &D" in the Los Angeles Catalytic Study (L.A.C.S.) and operated by the E.P.A. These sites are upwind and downwind and straddle the freeway between Sunset and Wilshire Boulevards.

After approval was obtained and access granted for use of the "C" site, two hi-volume air samplers (Staplex) were set up adjacent to the samplers maintained by E.P.A. The SwRI samplers were placed so that, relative to the freeway, they were downwind and in the same plane as the surface of the freeway. Samples were collected on Type A glass fiber filters without organic binders. Continuous collection took place until the rotameter on the sampler approached 40 cfm.

Table 2
Pertinent Socioeconomic and Demographic Characteristics of Volunteer Participants

	Total	Sex		Education Head of Household			Smoking History			Years of Residence* in Area or Occupation			Frequency of Change in Living Qtrs. (last 5 yrs)		
		M	F	0-12	13-16	Degree	Never	1 pk/da	1 pk/da	0-1	2-3	4+	0-1	2-4	5+
LOS ANGELES															
Age Group I	50	23	27	7	7	33	49	1	0	8	20	19	24	22	4
Age Group II	73	29	44	0	15	56	46	15	12	21	26	17	19	42	12
Age Group III	18	8	10	8	3	7	10	0	8	1	6	11	11	6	1
TOTAL	141	60	81	15	25	96	105	16	20	30	52	47	54	70	17
LANCASTER															
Age Group I	56	27	29	23	19	17	55	1	0	1	11	43	43	10	1
Age Group II	45	25	20	17	22	8	27	6	12	3	9	33	24	15	6
Age Group III	41	12	29	17	14	10	17	6	18	2	2	37	33	8	0
TOTAL	142	64	78	55	51	35	99	13	30	6	22	113	100	33	7
ONTARIO															
Age Group II	29	29	0	22	3	4	9	15	5	2	3	24	10	16	3
Age Group III	20	20	0	18	1	1	1	16	3	0	1	19	18	2	0
TOTAL	49	49	0	40	4	5	10	31	8	2	4	43	28	18	3
NEW JERSEY								Current Smoker No	Current Smoker Yes						
Age Group II	37	37	0	--	--	--		16	21	19	8	10	--	--	--
Age Group III	24	24	0	--	--	--		10	14	5	5	14	--	--	--
TOTAL	61	61	0					26	35	24	13	24			

*For New Jersey: Years worked for present employer

FIGURE 2

PERTINENT SOCIO-ECONOMIC AND DEMOGRAPHIC CHARACTERISTICS OF VOLUNTEER PARTICIPANTS

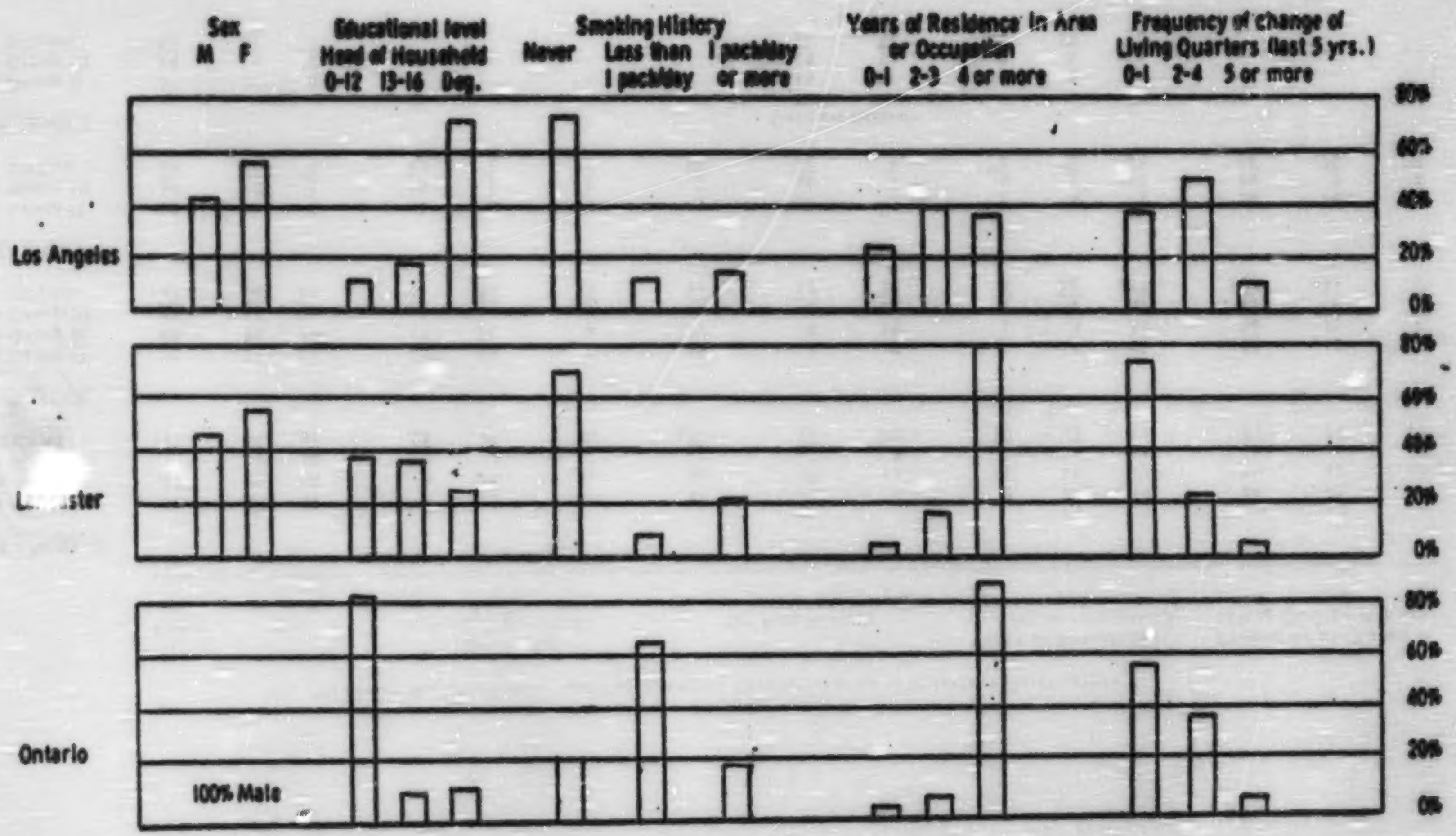


Table 3.
Analysis of Occupations of Volunteer Participants

Non-Occupationally-Exposed Participants

	Employed	Unemployed	Housewife	Student	Play/Nursery School	Pre-School	Retired
LOS ANGELES							
Age Group I	3	1	0	17	12	17	0
Age Group II	32	0	16	25	0	0	0
Age Group III	11	0	3	3	0	0	1
	46	1	19	45	12	17	1
LANCASTER							
Age Group I	0	0	0	46	4	6	0
Age Group II	38	2	3	1	0	0	0
Age Group III	32	1	3	0	0	0	5
	70	3	6	47	4	6	5

Occupationally-Exposed Participants

	Miners	Refiners	Electrowinners
ONTARIO			
Age Group II	9	3	15
Age Group III	6	8	8
	15	11	23
NEW JERSEY			
Age Group II	--	37	--
Age Group III	--	24	--
		61	

When this value was reached, a new, clean filter was then exchanged for the old filter with the particulate matter collected on it. The used filter was then folded in half with the sample on the inside. This previously numbered filter was then returned to its original plastic bag and sealed. A computer-printed label was then affixed to the bag and the identification number recorded in the log book on the data sheet. Each sample recorded had accompanying data that included initial and final times, rotameter readings and site location. Notation on wind direction was also made. Sample collection continued for 14 days. These samples were used for ambient air measurements of platinum and palladium. The objective was to collect particulate matter from as much air as possible (two samplers for 14 days) to insure that the maximum sensitivity could be achieved. The intent of the study was to report the limits of sensitivity as "less than" values if no platinum or palladium was detected.

In addition to the air sampling at site "C" of L.A.C.S., air samples were taken also at the UCLA Married Student Housing (MSH) on Sepulveda Blvd. The samplers were placed in the playground area next to MSH Community Center. This site was chosen because, as with the "C" site previously mentioned, it was also in the same plane as the freeway surface and more importantly was in the area where a large percenta of the study participants resided. The fenced-in playground area provided a secure spot for uninterrupted and undisturbed sample collection. Air collection times and procedures were the same as performed at the "C" site. These filters were used for ambient air lead measurements. Ambient air lead data from the LACS was to be used for most of the study area; however, it was decided that additional lead data would be needed for the UCLA MSH area, as this is some two miles from the LACS site.

During the Los Angeles air collection period, samples were also taken in Lancaster, California. Air samplers were placed in the backyards of homes within the community. Samples were collected continuously and until the pressure drop registered 40 cfm on the rotameter, at which time the filter was changed. These samples were used for Pt and Pd measurements. An additional air sampler was run to determine ambient air lead levels, and its filter was changed every 24 hours. Both types of samples, continuous and 24-hour, were collected over 14 days and ran concurrently with the Los Angeles samplers. Data reflecting sampling times and flow rates were noted and recorded in the log book. Calculation of the true and total air flow was performed using calibration sheets previously constructed for each air sampling unit.

During this 14-day air monitoring period, one day was set aside for soil sampling. Acid washed polyethylene containers were used for this purpose, and duplicate samples were taken at each site. Soil was sampled adjacent to sites "A" & "D". Surface soil samples were collected. Also, on opposite sides of (upwind and downwind) and within ten feet of the freeway, duplicate samples were taken. These sampling points were between sites "B" and "C"; however, they were much closer to the freeway than were the air sampling sites.

Soil samples were also taken at the UCLA MSH complex. Soil collected approximately 100 feet west of the freeway served as the control, as this point was upwind from the freeway. On the downwind side, duplicate samples were taken at 20, 100 and 300 feet from the freeway. The latter two distances, 100' and 300', are both within the confines of the MSH complex and approximate the boundaries of the complex perpendicular to the freeway. (Figure 8)

Samples in Lancaster were taken on a random basis within residential areas and near the hospital where many of the volunteers were employed. Each of the soil samples from Los Angeles and Lancaster had a computerized label placed on the container after collection which described the location and sampling point.

Water samples were collected in one liter acid-washed polyethylene containers. Samples were taken from tap water at the MSH complex, the Veterans Hospital (Wadsworth), and from various homes in the study areas both in Los Angeles and Lancaster. Again, each container had its own individual label affixed for easy referral at data analysis time.

Paint samples were collected from exterior surfaces of the MSH. Suitable samples were obtained by scraping the paint down to the surface using a knife. The paint chips were placed into polyethylene bags.

b. Mining

Environmental sampling was also performed at a mining and smelting complex in Sudbury, Ontario, Canada. The International Nickel Company (INCO) was most cooperative in allowing SwRI to conduct the survey at their facilities and fully assisted the survey team.

Air samples were collected at various points at the INCO facilities. The points were chosen based on discussions with the engineering personnel in order that probable sources of Pt and Pd could be ascertained before sample collection began.

Ambient air samples describing the background levels were collected outside near the INCO engineering building. Samplers were started and ran until the rotameter fell to approximately 40 cfm at which time a new filter was exchanged for the soiled filter. During the seven-day collection period, fog and misty conditions were present on three days and, consequently, the samplers were checked more often than usual.

Two samplers were operated in the precious metals building where the various metals are removed from the crushed ore slurry. This removal process is one of concentration in which some metals, especially Pt and Pd, are shipped in a residue form for processing at a subsequent facility. The air samplers were placed near probable sources of Pt and Pd in the room air during the concentrating of these metals. Particulate matter was collected on each of the filters until such time as the rotameter approached 40 cfm, and the filter was then changed.

Underground mining operations provided another air sampling point for Pt and Pd. The rationale for sampling air in the mines was to determine if the workers were inhaling these metals in the dust formed as a result of mining Pt and Pd ore and from the use of diesel engines operated with catalytic mufflers. The Institute survey team went down into the mines on a tour to observe mining operations and, more importantly, visit the sites where the air samplers were placed. The samplers were positioned near the various drilling, hauling and ore crushing processes and were in operation only during the hours of greatest activity which was during the day shift.

An air sampler was set up in the area where regeneration of the diesel muffler catalytic pellets was accomplished. The used pellets are screened to remove chaff and then are roasted in a regeneration unit at a temperature of 650°C to remove tar. During this roasting period, the air samples were taken.

Water and soil samples were taken during the same seven-day interval as were the air samples. A representative from INCO collected these samples.

c. Refineries

Sampling of the environment within a refinery in New Jersey was performed to characterize the particulate matter with reference to Pt and Pd. Two refineries of these precious metals were contacted to participate in the research study. One refinery performed their own sampling and analyses. The other refinery also collected samples, but the analyses were performed at the SwRI laboratories in San Antonio. The air in two areas of the second refinery complex was sampled. Staplex air samplers were suspended six feet from the floor near the return air flows in the salts recovery and refinery areas. The collection of the sample on preweighed 8" x 10" glass fiber filters took place for five consecutive work days. The filters were changed every 24 hours, and the total volume of air sampled was computed for each of the calibrated samplers. Each filter was subsequently vacuum-dried to achieve a constant weight before the weight of the particulate matter was determined. Before the filters were prepared for analysis, a section (15%) of each filter was quantitatively removed and set aside. This portion was sent to the refinery for their analysis. In addition to these sections of collected filters, an additional air sampler was also run by the company next to one of the SwRI samplers. Air sampling was performed concurrently with the biological collection from the human volunteers.

Environmental sampling other than air was not performed due to prior agreement with this company and concurrence of the Project Officer.

2. Study Participants

a. General Procedure

The conduct of a survey of this magnitude requires considerable advance planning.

Because of the variety and number of specimens required, an efficient labeling system was needed to ensure that all the samples were properly collected and processed. A computerized labeling system was used to preprint all labels necessary for sample collection and processing at a particular site. As an example, each participant had his own shopping bag labelled with his name and identification number. Inside the bag were the sample collection containers which had the participant's name, location (Los Angeles, Sudbury, etc.) identification number, sample type (urine, feces) and sample number (first or second sample). Prior to the first meeting with the participants, the collection kits were put together. These kits included two feces bottles and two urine bottles prelabelled with the above described label. The sample container kit was then handed out at the first meeting with the study participants.

Hair samples were collected from each participant in fulfillment of the sampling protocol. The accomplishment of this task was performed at the meetings when the volunteers came for blood collection. Professional barbers were used. Two types of hair samples were taken: long hair and short hair. The long hair was taken from the top and sides of the head using thinning shears. The short hair sample was taken from the nape of the neck where hair growth was most recent. Electric clippers were used to collect this sample, and a minimum of 1 gram of hair was required for each type of sample. It is obvious that the continued participation of the volunteer could easily be ended if the hair was cut improperly so as to alter the cosmetic appearance of the participant's hair. Therefore, before any hair was collected, each of the barbers was given verbal instructions on the type and amount of hair required and that the appearance of the participant's hair style must not be changed.

Blood collection was carried out by a qualified medical technologist under the supervision of a physician. While it was assumed that the medical technologist was familiar with blood collection procedures, a strong emphasis was made to preclude faulty technique. The technologist was advised as to the sources of contamination in the collection procedure.

Blood samples were collected by the vacutainer system using two 10-ml low lead, heparinized tubes as supplied by Becton and Dickinson. A suitable vein in the antecubital region was chosen, and the area was cleansed using a brisk mechanical scrubbing action with the alcohol prep. If the cleansed area came into contact with anything else before the sampling, the entire procedure was repeated. Similarly, sampling equipment was discarded if contaminated before use.

Experience in previous surveys indicated that a continuing effort was needed to alleviate any fears or hesitancy on the part of adults and especially the children in collection of blood samples. All procedures were thoroughly explained and questions answered before blood collection commenced. A concerted effort was made to insure that no trauma, either physical or emotional, was experienced by the volunteers. Although every effort was made to collect 10 ml of blood from young children, in some instances this was not possible. Some young children were quite small, and their veins were difficult to collect blood from even using specially designed syringes. As this study was on a voluntary basis, no undue chances were taken with these children, even if the primary difficulty was the child's noncooperation.

After the blood was drawn, the volunteer was instructed to place his thumb behind the elbow and with the remaining fingers wrap around the arm and hold the sterile gauze in place. The participant was then walked to the waiting area and observed for a few minutes. A tape strip bandage was then applied to prevent the puncture site from becoming infected. For the children, a special effort was made to compliment their behavior and to provide rewards of candy or balloons.

The blood collected in the vacutainers was immediately rotated for a few minutes to ensure that the heparin in the tubes would prevent coagulation from occurring. The blood sample was then poured into an acid-washed, 30-cc polyethylene bottle with the corresponding label attached and then immediately frozen. The urine samples were weighed and the specific gravity factor applied to yield the total volume. The bottle was then shaken to ensure a homogeneous sample and an aliquot poured into a 175-ml polyethylene bottle and made to 1% acetic acid. The corresponding label was placed on the bottle which was then put into an ice chest with dry ice. The feces sample was placed on dry ice as soon as it was handed to the survey personnel. Hair samples were kept at ambient temperature. All samples were held in their respective environments during shipment to, and storage at, the San Antonio laboratories.

b. Informed Consent

The volunteers selected for study were told about the project, its purpose, goals and possible connection to their way of life. The informed consent was presented to them, and it was explained that this form is a requirement of the U.S. Public Health Service whenever human subjects are employed in research. Emphasis was placed on the fact that the signing of this form in no way affected their right to withdraw from the program at any time. Each volunteer was verbally instructed as follows:

> "The informed consent form before you is a requirement of the U.S. Public Health Service regulations concerning use of human subjects. This form is for your protection. When it is completed by your signature and my signature, it will serve as a record that I, as a Project Director, have been present to answer any of your questions regarding the project that I have described, the purposes and intent of the program, as well as a description of any inconveniences, discomforts, and potential risks that may be involved, and I have provided you with a description of the benefits expected. I have also assured you that you are free to withdraw your consent and discontinue your participation in

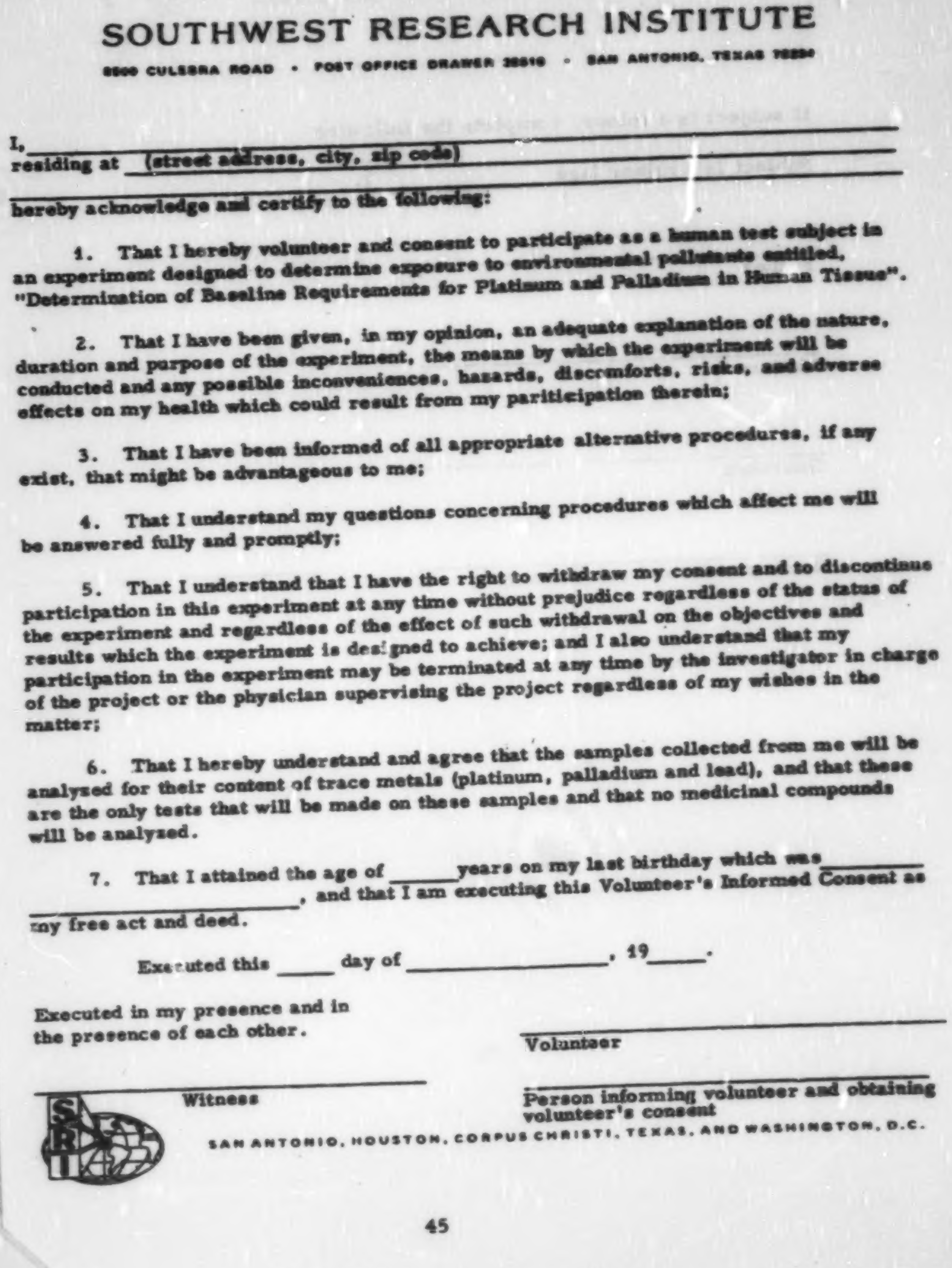
the project or activity at any time you wish. I also wish to assure you that your identity in this survey will not be disclosed. If you feel that I have accomplished these to your satisfaction and that you are willing to participate in the survey, please sign the informed consent."

The volunteers were then asked to sign the consent form if they felt that the goals of the project, any possible discomfort to them and non-disclosure aspects had been explained to their satisfaction. The consent form thus signed by the volunteer was then countersigned by the project director as the person who informed them. Another participant in the survey acted as a witness to the above signatures. At present, these signed informed consents are on file at SwRI in the office of the principal investigator. Access to the names of these volunteers has been limited to the principal investigator and his project staff. A copy of the form used for informed consent is shown in Figure 3.

c. Information Sheets

After the informed consents were completed, the participants in the study were given a detailed explanation of the schedule for collection of samples. Sample containers for urine and feces collections were then handed out. Usually, a small group (5-10 people) had the collection procedures explained to them, and in this way the time spent

Figure 3. VOLUNTEER'S INFORMED CONSENT



SOUTHWEST RESEARCH INSTITUTE

8500 CULEBRA ROAD • POST OFFICE DRAWER 28510 • SAN ANTONIO, TEXAS 78284

I, ______________________________

residing at (street address, city, zip code) ______________________________

hereby acknowledge and certify to the following:

1. That I hereby volunteer and consent to participate as a human test subject in an experiment designed to determine exposure to environmental pollutants entitled, "Determination of Baseline Requirements for Platinum and Palladium in Human Tissue".

2. That I have been given, in my opinion, an adequate explanation of the nature, duration and purpose of the experiment, the means by which the experiment will be conducted and any possible inconveniences, hazards, discomforts, risks, and adverse effects on my health which could result from my paritiicipation therein;

3. That I have been informed of all appropriate alternative procedures, if any exist, that might be advantageous to me;

4. That I understand my questions concerning procedures which affect me will be answered fully and promptly;

5. That I understand that I have the right to withdraw my consent and to discontinue participation in this experiment at any time without prejudice regardless of the status of the experiment and regardless of the effect of such withdrawal on the objectives and results which the experiment is designed to achieve; and I also understand that my participation in the experiment may be terminated at any time by the investigator in charge of the project or the physician supervising the project regardless of my wishes in the matter;

6. That I hereby understand and agree that the samples collected from me will be analyzed for their content of trace metals (platinum, palladium and lead), and that these are the only tests that will be made on these samples and that no medicinal compounds will be analyzed.

7. That I attained the age of ______ years on my last birthday which was __________ __________________, and that I am executing this Volunteer's Informed Consent as my free act and deed.

Executed this _____ day of ________________, 19_____.

Executed in my presence and in the presence of each other.

____
Volunteer

____
Witness

____
Person informing volunteer and obtaining volunteer's consent

SAN ANTONIO, HOUSTON, CORPUS CHRISTI, TEXAS, AND WASHINGTON, D.C.

VOLUNTEER'S INFORMED CONSENT
(page 2)

If subject is a minor, complete the following.

Subject is a minor (age ______________).

____
Father

____
Mother

____
Guardian

______________________________ ______________________________
Other person and relationship

at this meeting could be kept to a minimum. It was emphasized to each volunteer that accurate information could only be obtained if directions were followed completely. Incomplete sampling would produce incomplete information, and therefore the success of the research project depended on their complete cooperation.

The urine collection began in the evening after supper, generally between 6 and 8 PM. Prelabeled, 2-liter wide-mouth polyethylene bottles were given to each participant for the urine collection. These containers had been cleaned in an acid bath containing 4N HCl and 3N HNO_3 for eight hours, then rinsed at least six times with deionized water and finally dried in a laboratory oven. The subjects were told to collect urine through the next morning. The sample was then brought to the place designated for blood collection or dropped off at a collection point. The second sample collection began that evening after supper and continued until the following morning.

Instructions for fecal specimens were also given. Again, the volunteers were cautioned against putting anything into these specially cleaned containers other than their own feces. Toilet paper or urine were to be avoided. During the same period as the urine collection, the volunteers were told to collect all of their fecal specimens. No restriction was placed on the volunteer's diet. Verbal instructions for the proper collection for each of the samples was supplemented by a printed instruction sheet included in the bag with the containers given to each individual.

When each subject had completed the sample collections, he was paid for his participation. Each volunteer was told that he would receive a summary of the results. Individual values were not to be given.

The procedure used at the refineries for collection of samples differed somewhat from those of the baseline and mining areas. At both refineries, blood and urine samples were collected in conjunction with an annual physical examination of the employees. Collections were carried out by the companies. At one of the refineries, an information form was filled out by each employee listing name, age, sex, job title, length of employment with the company, shift worked, and smoking habits. An identification number was assigned to each employee and this number incorporated on each of the samples collected.

The procedures used at this refinery were as follows: Acid-washed urine collection containers showing participants' names were handed out to each volunteer. They were given verbal and written instructions on the proper collection of samples. Shift workers from the three shifts at the plant volunteered; thus, the collection period varied according to shift. For the day shift, they were told to begin collection of their samples in the evening (generally between 6:00-9:00 PM). Collection continued through the night and included the first sample upon arising in the morning. The second shift (4:00 P.M. to 12:00 Midnight) began their collection after work and continued until the first specimen after arising was collected. For the personnel of the third shift

(11:00 P.M. to 7:00 A.M.), the first specimen after rising was collected. In each case, the workers were asked to bring the urine samples to the nurse's station after collection was completed. Each specimen was subsequently weighed, and an aliquot (maximum of 175 ml) was acidified to 1% acetic acid. These aliquots were then immediately frozen. An additional aliquot of each sample was also prepared for the company in the manner prescribed above.

Collection of blood was performed by medical technologists employed at a local hospital.

Blood collection took place at the plant and during working hours with the employees being scheduled at the convenience of the plant's production schedule. For the day-shift personnel, appointments were made for every 10 minutes, and this schedule was posted as a reminder to each participant. Blood sampling was begun at 1 P.M. and continued until all volunteers from the day shift had their blood drawn. However, before blood collection began, each employee was instructed to wash his arms thoroughly with soap and water lest any trace amount of Pt and Pd contaminate his blood sample. If the arm was still dirty after the medical technologist had washed the antecubital area with an alcohol swab, the arm was rewashed with additional soap and water. Standard blood drawing techniques were used with the vacutainer system employing two 10-ml heparinized, low-lead vacutainers. The blood in each of the two low-lead vacutainers was poured into acid-washed 30-cc polyethylene bottles as soon as practical after collection. One blood sample was frozen and the other retained by the refinery. The SwRI samples were shipped frozen in dry ice to San Antonio and kept frozen until analysis.

Autopsy samples were collected in Los Angeles and in Sudbury. Twenty-five gram samples of muscle, liver, kidney, spleen, lung and fat were collected by a pathologist in a hospital in the area. Unsuccessful attempts were made to secure autopsy samples from accidental deaths through Medical Examiner's offices. Each pathologist was given sample containers with a label that was to be filled in for information such as age, sex, ethnic origin, cause of death and smoking history if known. The pathologists were advised as to the intended purpose of these samples, and each was instructed on the precautions to follow to prevent contamination. All samples were frozen as soon as possible following collection and kept frozen until analyzed.

Ten autopsy cases (5 male - 5 female) were collected in Los Angeles, and ten were collected in Sudbury (all male). The autopsy cases in Los Angeles were from persons of different ages (young to elderly) that resided in Los Angeles prior to death. The autopsy cases from Sudbury were restricted to individuals that had been employed as miners, ore processors, etc. in the mining operations in Sudbury.

D. Analytical Methods

1. Literature Review

Review of the literature prior to 1974 revealed very few references to Pt or Pd concentrations in biological samples. Generally, where references were made to Pt or Pd, neutron activation analysis was the only method able to estimate the concentration present.(2)

There are a number of references in the literature for Pt and Pd analysis on metallurgical, geological and other types of samples using atomic absorption spectrophotometry; however, the levels of the two metals are much higher in these samples than in biological samples.

Increased interest in Pt and Pd over the last two years has produced several recent papers dealing specifically with Pt and Pd in biological samples. A paper by Yoakum, Stewart and Sterrett(3) gave an emission spectrochemical method to determine Pt, Pb and Mn in rat tissues. These investigators stated that the emission spectrochemical method and flameless atomic absorption methods could not reach a level of sensitivity sufficient to quantitate residual concentrations of Pt in tissues without preconcentration treatment.

LeRoy(4) stated that, to determine Pt in one gram of wet tissue by the graphite analyzer, there would have to be a minimum concentration of 0.25 ppm for reproducible results. This was based upon direct injection of the digested tissue into the graphite analyzer. LeRoy also mentioned the use of aliphatic secondary amines (in xylene) as extractants for preconcentrating Pt and Pd prior to analysis. He stated that methyl isobutyl ketone (MIBK) could be used to extract Pt but did not recommend it.

An excellent review of analytical methods for determining Pt and Pd in biological tissue by Bumgarner and Yoakum(5) summarized the situation regarding "flameless" atomic absorption analysis by saying a preconcentration scheme would still be necessary.

Analysis of Pt and Pd using the graphite analyzer ("flameless") and atomic absorption spectrophotometry (AAS) has been reported on aqueous solutions both directly and by extract.(6-8) Adriaenssens and Knoop(9) have reported the optimal conditions for analysis of three noble metals (including Pt) in the graphite analyzer. The reported sensitivity and detection limit for Pt were 1 ng and 1.1 ng , respectively.

Guerin(10) reported some interferences that can affect the analysis of Pt and Pd in the graphite analyzer. He also mentioned the extraction of Pt and Pd using Aliquat 336 in MIBK from HCl solution. Guerin said there was no solvent enhancement effect as there is with flame analysis using organic solvents. The reported absolute detection limit using a 10µl injection of the extract was 0.005 ng Pd and 0.05 ng Pt.

Janoušková, Nehasilová and Sychra(11) examined the effect of 19 elements and 6 acids on the graphite furnace determination of Pt. They found that only ruthenium, strontium and nitric acid interfere. The reported sensitivity was 0.8 ng for 1% absorption.

2. Instrumentation

All analyses aru performed on a Perkin-Elmer Model 306 Atomic Absorption Spectrophotometer modified (Perkin-Elmer Optical Modification Kit No. 040-0286) to reduce the "light scattering" effect caused by the graphite furnace. A Deuterium arc background corrector is routinely used to compensate for non-specific background absorption. Absorption peaks are recorded with a Perkin-Elmer Recorder Model 056 with a 10 mv range.

Flameless analyses are done with a Perkin-Elmer HGA-2000 Graphite Furnace. Flame analyses are by aspiration of the sample into an air-acetylene flame using a 3-slot burner head.

Calculation of analytical curves (method of additions) and determination of unknown sample concentrations are done on a Hewlett-Packard Programmable Calculator Model 9810A.

Ashing of tissue samples for Pb determination is performed on a LTA505 low temperature asher manufactured by LFE Corporation, Waltham, Massachusetts.

Evaporation of urine and water samples is carried out with a Rotavapor-RE/A, Brinkmann Instruments, Inc., Westbury, New York.

3. Reagents

All reagents are analytical grade unless otherwise indicated.

Atomic absorption standard solutions (1,000 ppm) for Pt and Pd are the H_2PtCl_6 and $PdCl_2$, respectively, from Ventron Corp., Alfa Products, Danvers, Massachusetts. Atomic absorption standard for Pb (1,000 ppm) is from Fisher Scientific Co., Pittsburgh, Pennsylvania.

4. Selection of Analytical Methodology

Several important criteria were considered in the development of methodologies for Pt, Pd and Pb analyses of biological material.

(a) Since the expected concentration of Pt and Pd in the samples would be very low, some preconcentration procedure would be needed.

(b) The methods developed had to be adaptable to large numbers of samples.

(c) The method must be fast, simple, and accurate.

(d) If possible, the sample workup would be for all three elements to avoid duplication of effort.

(e) The time available for methodology development would be limited.

The final criterion, being the most severe, limited the development to selecting procedures from the literature and adapting them to biological samples and atomic absorption analysis.

5. Platinum and Palladium Methodology

a. Extraction Procedure

The above restrictions placed on the analytical methods development of Pt, Pd and Pb directed the main emphasis to finding a suitable extraction procedure which would quantitatively remove Pt, Pd and Pb from the sample matrix.

Ammonium pyrrolidine dithiocarbamate (APDC) chelation with subsequent extraction of the metal complexes into methyl isobutyl ketone (MIBK) was tried on aqueous spike solutions. Very erratic results were obtained with Pt, but Pb and Pd extracted very well at pH 5.0. Recoveries of Pd ranged from 68 to 87%.

Extraction of the stannous-chloro complexes of Pt with MIBK or ethyl acetate gave recoveries of 80 to 120% at spike concentration of 0.8 ppm but only 40-50% at 0.1 ppm. Pd and Pb were not extracted under these conditions.

The extraction of Pt and Pd stannous-chloro complexes with high molecular weight amines (HMWA) appeared to fulfill most of the requirements listed earlier for an acceptable extraction procedure. Lead, however, did not extract under the conditions used for Pt and Pd. Our method was patterned after those of Khattak and Magee.(12,13)

Biological samples have to be digested or ashed prior to determining the analyte metal(s), and this provides a convenient means of extracting with a HMWA. The digest or ash is either in, or solubilized in, an acid solution, therefore time-consuming pH adjustments are unnecessary, since the amine functions in an acidic environment. The overall reaction for this type of extraction is:

$$RNH_{2(org)} + H^+A^-_{(Aq)} \rightleftharpoons [RNH_3{}^+A^-]_{(org)} \tag{1}$$

$$n[RNH_3{}^+A^-]_{(org)} + [MX]^{n-}_{(Aq)} \rightleftharpoons \left([RNH_3{}^+]_n\ [MX]^{n-}\right)_{(org)} + nA^-_{(Aq)} \tag{2}$$

where $H^+A^-_{(Aq)}$ is HCl and $MX^{n-}_{(Aq)}$ represents the stannous-chloro complex of Pt(IV) or Pd(II).(14)

The procedure for extraction is essentially the same for all types of samples. The sample is either digested with acids or ashed in a muffle furnace. Samples digested with acid are evaporated to 1 to 2 ml on a hot plate under N_2 and then reconstituted and evaporated three times with 5 ml of concentrated HCl. Following the last evaporation, the sample is cooled and transferred to an extraction vessel using 3 N HCl.

Ashed samples are solubilized with aqua regia, evaporated to 1-2 ml on a hot plate under N_2 and then carried through the evaporation-reconstitution procedure described above.

Once the sample has been transferred to an extraction vessel (15-20 ml screw-cap Pyrex centrifuge tube), the sample is adjusted to approximately 10 ml with deionized water or 3 N HCl. The solution should be approximately 3 N HCl for extraction.

One milliliter of 25% $SnCl_2$ solution (in 3 N HCl) is then added, and the sample is vigorously shaken for 30 seconds. A 1-ml aliquot of 0.02 M tri-n-octylamine (xylene solution) is added, and the sample is shaken for 30 minutes followed by centrifuging for 15 minutes at 3,000 RPM. The octylamine layer (top) is removed with an Eppendorf pipet and placed in a 4-ml screw-cap vial.

A quick second extraction of the sample is carried out with 0.5 ml of xylene, and this is added to the original extract.

The extract is evaporated to dryness under N_2 on a hot plate using low heat. Once the extract is dry, it is capped and stored until ready for analysis. Just prior to analysis, the sample is reconstituted with 0.1 ml (100 µl) xylene and mixed well. A 5-µl or 10-μl aliquot of the extract is injected into the graphite analyzer (HGA-2000) for determination of Pt and Pd.

The acid concentration of the extract solution effects recovery of both Pt and Pd. Figure 4 illustrates that increasing the acid concentration above 0.5N causes a decrease in recovery of Pd, while an increase above 8N causes a marked decrease in recovery of Pt. An approximately 3N HCl extract was decided upon, since it provided good recovery of both Pt and Pd and was convenient to use for extracting a large quantity of samples.

Some other elements were investigated as to their effect upon the extraction of Pt and Pd. Table 4 shows that only Cu at 2,000 ppm proivded a significant effect upon a 50 ng Pt (1 ppm) extract signal.

Pd (37.5 ng) (0.075 ppm) was seriously affected by Fe (2,000 ppm) and Cu (2,000 ppm) as illustrated by Table 4. Mn also enhanced the Pd signal.

Another source of interference with the Pt and Pd extraction is the concentration of the $SnCl_2$ solution used to form the anionic species prior to extraction. Figures 5 and 6 illustrate the effect upon Pt and Pd in a 3N HCl solution. There is a marked decrease in the response obtained from 50 ng of Pt extract and 37.5 ng of Pd extract as the concentration of the $SnCl_2$ solution is increased. This effect was not observed until late in the study, and, therefore, the 25% $SnCl_2$ concentration was used.

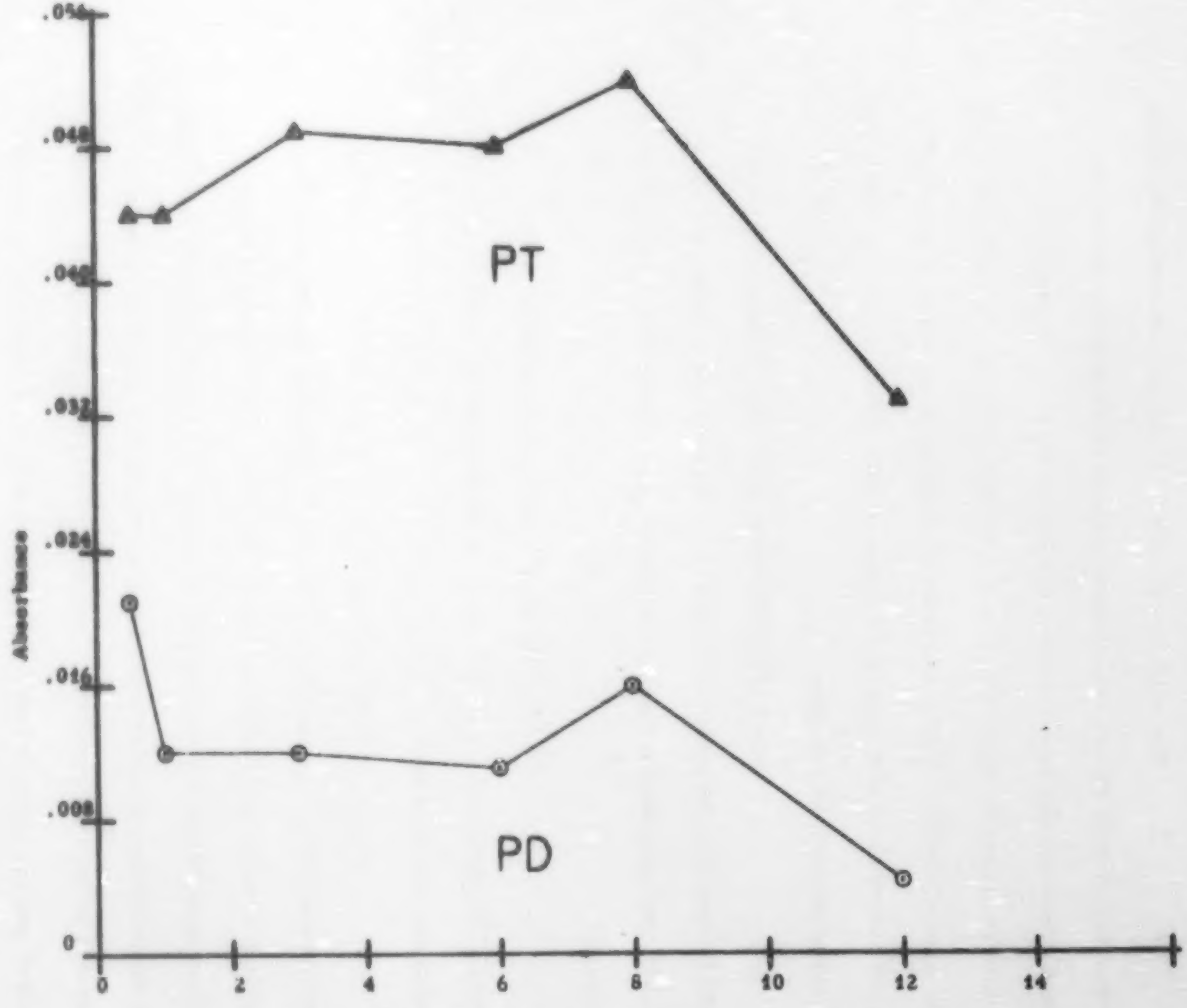


FIGURE 4. EFFECT OF ACID CONCENTRATION UPON HMWA EXTRACTION OF Pt and Pd.

TABLE 4. EFFECT OF ELEMENTS UPON EXTRACTION OF Pt and Pd FROM 3 N HCl

Element	Concentration ppm(1)	Pt(2)	Pd(3)
Fe	2000	0(4)	++(4)
Mn	500	0	+
Cu	2000	+	++
Pb	1000	0	0
Cd	500	0	0
Zn	2000	0	0

---

(1) Concentration in 3M HCl solution Pt and Pd extracted from.

(2) Concentration of Pt = 1 ppm (50 ng of extract analyzed).

(3) Concentration of Pd = 0.075 ppm (37.5 ng of extract analyzed).

(4) + = enhancement of signal
0 = no effect.

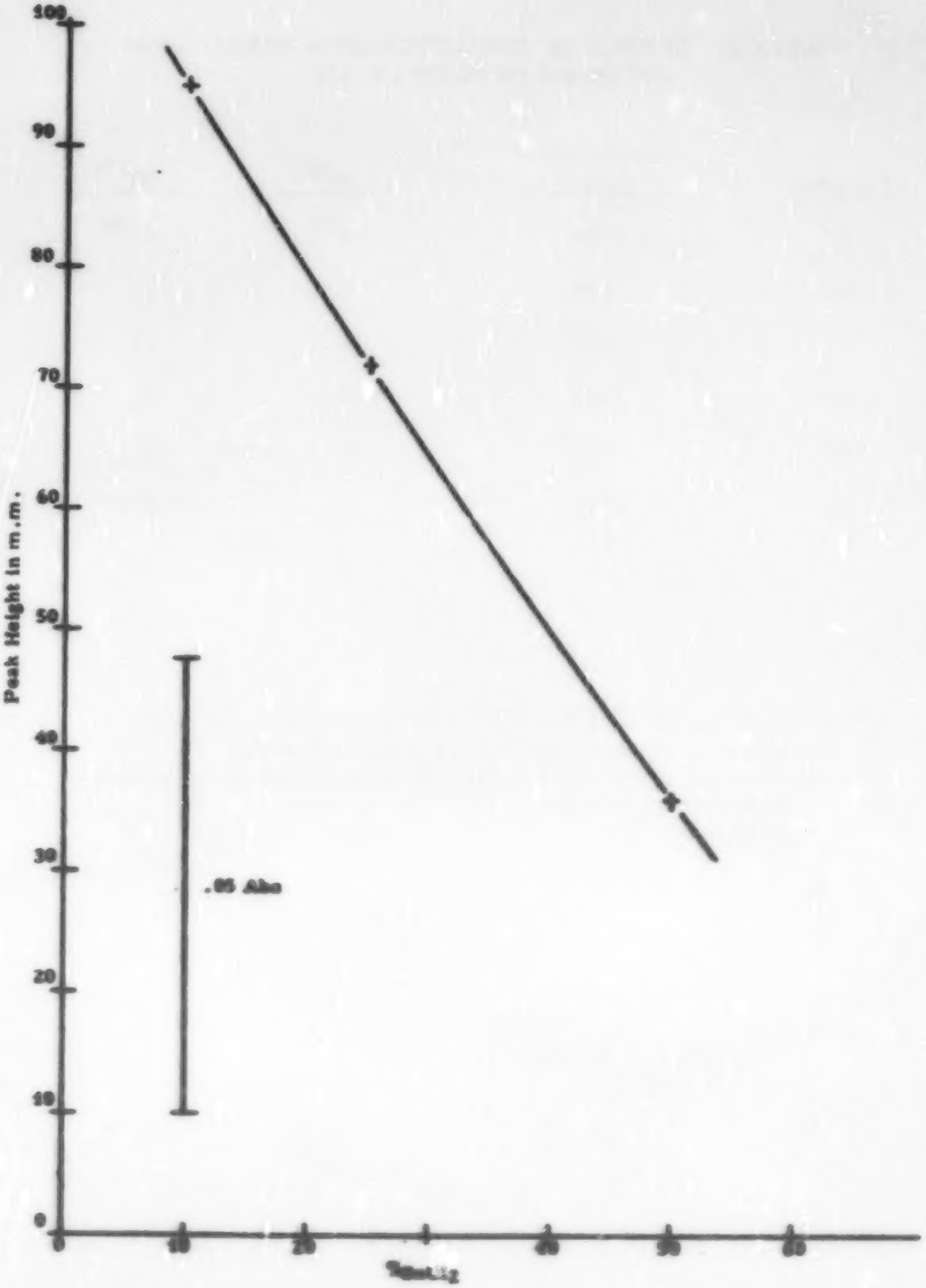


FIGURE 5. EXTRACTION OF Pt (25ng) FROM 3N HCl USING VARIOUS CONCENTRATIONS OF $SnCl_2$ SOLUTION (3 N HCl)

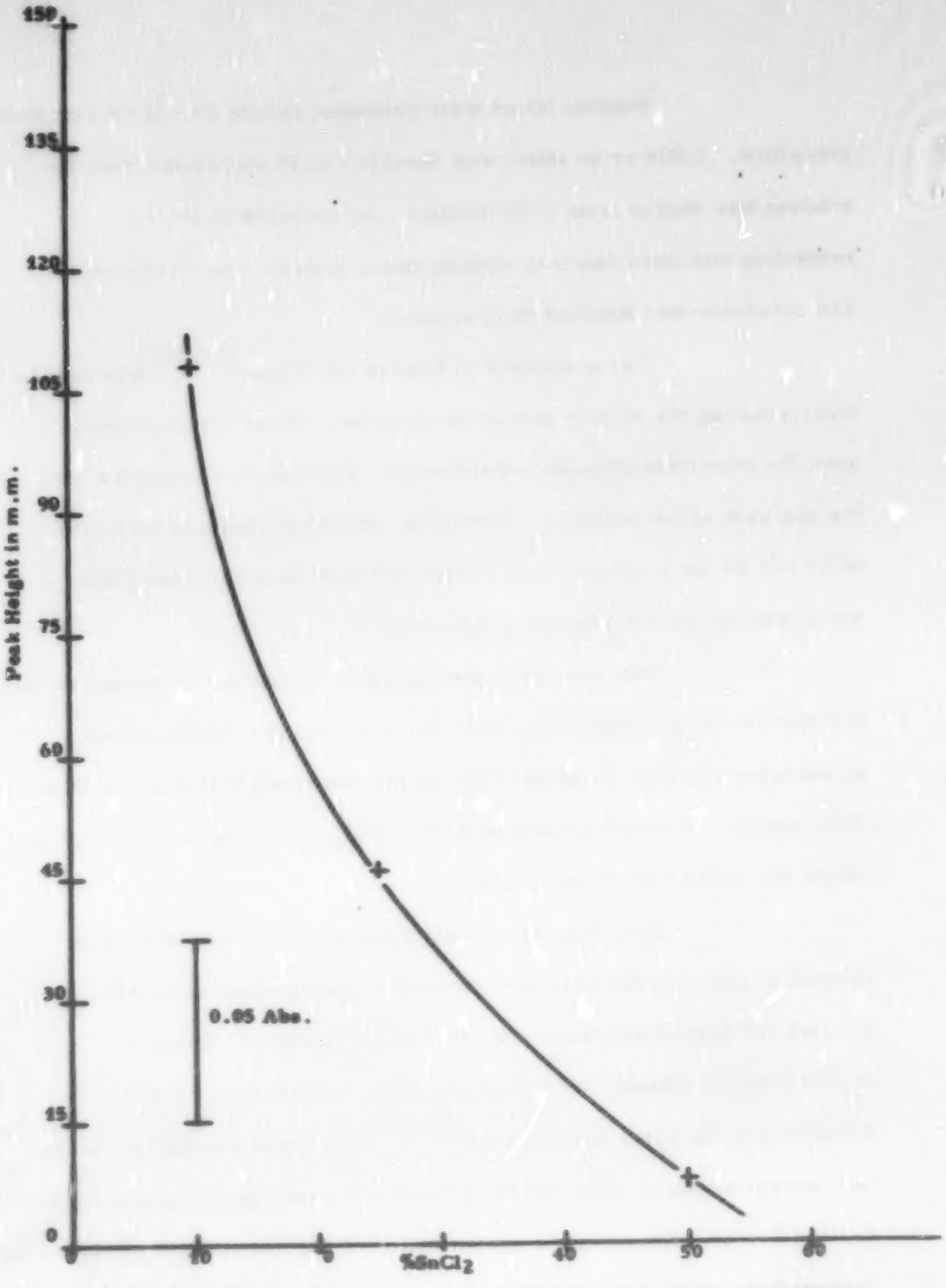


FIGURE 6. EXTRACTION OF Pd (12.5 ng) FROM 3N HCl USING VARIOUS CONCENTRATIONS OF SnCl$_2$ SOLUTION (3N HCl)

Shaking times were examined for the Pt and Pd extraction procedure. Little or no effect was observed on Pt extraction when the solution was shaken from 5-60 minutes. An increase in the Pd extraction was observed with shaking times greater than 5 minutes. The maximum was reached in 15 minutes.

The procedure of Khattak and Magee (12, 13) was followed closely during the earlier part of the program, but as improvements upon the extraction procedure were made, they were incorporated into the analysis of the samples. Therefore, improved limits of detection of Pt and Pd for a sample matrix from different locations (see Table 5) were realized as the program progressed.

The extraction procedure for Pt and Pd is limited by the fact that the anionic exchange liquid tri-n-octylamine (TOA), creates an excessive amount of "smoke" during the atomization step in the HGA-2000. This restricts the total amount of extract that can be analyzed and thereby limits the sensitivity of the method.

Reducing the concentration of the anionic liquid is a method of reducing the excessive "smoke". The original procedure of Khattak and Magee called for a 0.2M TOA (in benzene). Below a 0.02M TOA (in xylene), the extraction of Pd became very erratic. According to Davidson and Jameson, (15, 16) this would be expected since the concentrations of other anions present will limit the extraction of the desired anions. Reducing the concentration of the anionic liquid would, in effect, present fewer available exchange sites for which the analyte anionic species could compete.

TABLE 5. LIMITS OF DETECTION OF Pt and PD IN BIOLOGICAL SAMPLES(1)

Sample Type	Study Area	Pt ppm	Pd ppm	Sample Size
Blood	Baseline	0.031	0.009	10 ml
	Mining	0.0014	0.0004	15 ml
	Refinery	0.0014	0.0004	15 ml
Urine	Baseline	0.006	0.003	1000 ml composite
	Mining	2×10^{-5}	7×10^{-6}	1000 ml composite
	Refining	0.0001	0.0002	150 ml
Hair	Baseline	0.05	0.02	11.5 grams composite
	Mining	0.0019	0.0006	11.5 grams composite
Feces	Baseline	0.002	0.001	300 grams composite
	Mining	7×10^{-5}	2×10^{-5}	300 grams composite
Liver	Baseline Mining	0.00024	0.0006	55 grams wet tissue
Kidney	Baseline Mining	0.0025	0.0067	5 grams wet tissue
Spleen	Baseline Mining	0.0013	0.0033	10 grams wet tissue
Lung	Baseline Mining	0.0013	0.0033	10 grams wet tissue
Muscle	Baseline Mining	0.0009	0.0022	15 grams wet tissue
Fat	Baseline Mining	0.0013	0.0016	10 grams wet tissue

---

(1) 2X background noise = limit of detection.

The absolute amounts of Pt and Pd, which may be quantitated on the Perkin-Elmer Model 306, are 1.07 ng and 0.33 ng, respectively. Improvement in the limit of detection therefore necessitated using larger sample quantities. This was achieved by compositing a large number of small samples to get one larger sample. Compositing of samples was done for hair, urine, feces, and air. Table 5 gives the limit of detection of Pt and Pd for each sample matrix and location. The limit of detection for the composite samples is based on the absolute amounts of Pt and Pd detectable with the P-E 306 and the size of the composite used.

b. Biological Samples

(1) Blood

Whole blood samples were digested with $HNO_3:HClO_4$ (70:30) in a Vycor beaker on a hot plate (150°C) with a flow of N_2. Table 5 gives the volume of blood analyzed from each sampling site. The blood was evaporated to 1-2 ml and reconstituted 3X with 5 ml of concentrated HCl. Following the last evaporation, the samples were removed from the hot plate and allowed to cool before rinsing into an extraction vessel with 3N HCl. The extraction procedure outlined earlier for Pt and Pd was followed to remove these elements from the digested matrix.

The blood digests from the baseline study were extracted with 0.2M TOA (in benzene). Only 3/5 of the extract solution could be recovered for evaporation-reconstitution because of the solubility of benzene in the aqueous phase. The mining (Sudbury) and refinery blood digests were extracted with 0.02M TOA (in xylene). All of the organic extract was recovered for subsequent evaporation-reconstitution as outlined in the extraction procedure.

Recovering all of the TOA extract, a substantial improvement in the limit of detection was realized (Table 5). Precision also improved for Pt and Pd analysis.

(2) Urine

Composites of urine from each sampling site (except the refinery) were made from the individual overnight samples. Composites were approximately 1 liter in volume.

A rotary evaporator was used to reduce the composite urine samples to dryness. The urine residue was solubilized with aqua regia (50 ml) and rinsed into a Vycor beaker. The sample was evaporated to dryness on a hot plate (150°C) under N_2. The dried residue was then ashed in a muffle furnace at 500°C using $Mg(NO_3)_2$ as an ashing aid. The ash was then solubilized with aqua regia and again evaporated to near dryness on a hot plate (150°C) under N_2. The sample was reconstituted-evaporated with 5 ml of concentrated HCl. Following the last evaporation, the sample was transferred to an extraction vessel with 3N HCl and extracted according to the procedure outlined earlier for Pt and Pd.

Table 6 gives the spike levels used with the composite samples.

TABLE 6. Pt and Pd SPIKE LEVELS OF COMPOSITE SAMPLES

Sample	Quantity of Sample Analyzed	Microliters of Spike Solution Used*	Concentration in ppm	
			Pt	Pd
Urine	1 liter	500	0.0010	0.0005
		100	0.0002	0.0001
Feces	300 grams	500	0.0033	0.0017
		100	0.0007	0.0003
Hair	11.5 grams	50	0.0087	0.0043
		100	0.0174	0.0087
		200	0.0348	0.0174

---

*Spike solution: 2 µg/ml Pt and 1 µg/ml Pd.

(3) Hair

Composites of hair were made from the "long hair" samples collected at each sampling site. The composite samples consisted of about 12 grams of hair (see Table 6).

The hair was washed with 0.12M sodium lauryl sulfate solution and rinsed 3X with deionized water, followed by an isopropyl alcohol wash and by three rinsings with deionized water. The washed hair was then transferred to a polyethylene beaker and placed in an oven at 60°C to dry.

The dry hair sample was weighed into a Vycor beaker, and 30 ml of $HClO_4:HNO_3$ (1:1) was added. The sample was allowed to stand at room temperature 1-2 hours before placing on a hot plate (150°C) for evaporation-digestion. The volume of sample digest was reduced to 1-2 ml and reconstituted-evaporated 3X with concentrated HCl. Following the last evaporation, the sample was rinsed into an extraction vessel with 3N HCl and extracted by the previously outlined procedure for Pt and Pd.

(4) Feces

Fecal samples were composited for the baseline study and the mining study. The composites ranged from 300g to 500g (Table 6). The samples were partially digested with concentrated HNO_3 overnight in polyethylene jars. Following this partial digestion, the samples were further digested by adding small aliquots to a 400-ml Teflon beaker on a hot plate (125-150°C) and digesting-evaporating until all of the sample had been completely digested. The digestion was continued by adding HNO_3 until a clear amber solution remained. The solution was then evaporated down until solids were observed forming in the digest. Then 10 ml $HClO_4$ was carefully added and the digestion continued until 2-3 ml remained. The sample was then filtered through a glass-fiber filter with rinsing of 6N HCl. The filtrate was evaporated to near dryness on a hot plate and reconstituted-evaporated 3X with concentrated HCl. Following the last evaporation, the sample was transferred to an extraction vessel and extracted by the procedure given for Pt and Pd.

(5) Tissues

Tissue samples from the baseline and mining studies were homogenized using a VirTis "45" Homogenizer with stainless steel blades. Approximately 5-55 grams of tissue (wet) were homogenized, depending upon the type (see Table 5).

The tissue homogenates were weighed into a Vycor beaker and placed in a vacuum oven at 40-50°C overnight. The dry samples were then mixed with $Mg(NO_3)_2$ ashing aid and placed in a muffle furnace at 500°C. The samples were ashed until a white ash remained. The ash was solubilized with aqua regia and evaporated-reconstituted 3X with concentrated HCl. Following the last evaporation, the sample was transferred to an extraction vessel with 3N HCl. Extraction followed the procedure outlined earlier for Pt and Pd.

c. Environmental Samples

(1) Air Samples

Air samples from the baseline, mining and refinery studies were each composited (Table 7). The composited glass-fiber filters (20.3 x 25.4 centimeters) were cut into approximately 1-cm squares, added to a 2-liter boiling flask, and 100-250 ml of aqua regia was added. The amount of acid added depended upon the number of filters composited. Samples were refluxed for 24 hours, filtered through glass-fiber filters, and the filtrates were evaporated to several milliliters on a hot plate (150-200°C) under N_2. The remaining sample was then reconstituted-evaporated 3X with concentrated HCl. Following the last evaporation, the sample was transferred to an extraction vessel with 3N HCl. Extraction of Pt and Pd followed the procedure given earlier.

(2) Soil Samples

Soil samples were dried in an oven (60°C) for 48 hours before being ground with a mortar and pestle. Five grams of the dried, ground soil was weighed into a 250-ml Vycor beaker and digested with 50 to 150 ml of aqua regia on a hot plate (200°C) with constant stirring. The samples were removed from the hot plate, cooled, and filtered with a glass-fiber filter. The filtrate was collected in a Vycor beaker, evaporated under N_2 to 1-2 ml and reconstitute-evaporated 3X with 5 ml of concentrated HCl. Following the last evaporation, the sample was rinsed into an extraction vessel with 3 N HCl and extracted by the procedure given earlier for Pt and Pd.

TABLE 7. LIMITS OF DETECTION OF Pt and Pd IN ENVIRONMENTAL SAMPLES

Sample Type	Study Area	Pt	Pd	Sample Size
Water	Baseline	8×10^{-5} ppm	2.4×10^{-5} ppm	250 ml sample
	Mining	5×10^{-5} ppm	1.5×10^{-5} ppm	400 ml sample
Soil	Baseline	0.0008 ppm	0.0007 ppm	10 g dry sample
	Mining			
Air	Baseline exposed	0.05 pg/m^3	0.062 pg/m^3	47424 m^3 composit
	Baseline control	0.11 pg/m^3	0.033 pg/m^3	9988 m^3 composite
	Mining	0.003 μg/m^3	0.003 μg/m^3	2111 m^3 composite
	Refinery	0.003 μg/m^3	0.003 μg/m^3	2111 m^3 composite

(3) Water Samples

Up to 400 ml of water was used in the determination for Pt and Pd. The sample volume was reduced to less than 10 ml in a rotary evaporator under reduced pressure and 70°C heat. Using approximately 25 ml of aqua regia, the sample was rinsed into a Vycor beaker and digested-evaporated to 1-2 ml, under N_2, on a hot-plate (150°C). The sample was reconstituted-evaporated 3X with 5 ml concentrated HCl and transferred to an extraction vessel with 3 N HCl. Extraction of Pt and Pd followed the procedure given earlier.

6. Lead Methodology

a. Biological Samples

(1) Blood

The procedure of Hwang, Ullucci and Mokeler(17) using modifications from the method of Mitchell, Ryan and Aldous(18) was used to determine the Pb concentration in whole blood samples.

Using an Eppendorf pipet, a 1.0-ml aliquot of whole blood was transferred into a 5-ml centrifuge tube. One milliliter of a hemolyzing-chelating solution consisting of a 5% Triton X-100 (octylphenoxypolyethoxyethanol, Rohm and Haas, Philadelphia, Pa.) solution containing 2% ammonium pyrrolidine dithiocarbamate (APDC) was added, and the sample was mixed vigorously for 5 minutes and allowed to stand 10 to 15 minutes to ensure complete hemolysis of the blood; this was followed by the addition of 1.0 ml of water-saturated MIBK. The sample was then shaken for 3 minutes and centrifuged for 5 minutes at 3,000 RPM. The organic layer was then analyzed for Pb by injecting 10-µl aliquots into the HGA-2000 graphite furnace.

(2) Urine

The procedure used for urinary Pb determinations was based upon that of Kubasik and Volosin.(19)

A 10-ml aliquot of acidified urine (1% acetic acid added as a preservative) was pipetted into a 25-ml centrifuge tube. Using NaOH, the pH was adjusted to 7.0, and 5 ml of tris(hydroxymethyl)-aminomethane buffer (pH 7.0) was added. One milliliter of a 1% APDC solution was added along with 1.0 ml of water-saturated MIBK. The sample was mixed for 10 minutes and then centrifuged for 10 minutes at 3,000 RPM, and the organic layer was removed for Pb analysis by injecting aliquots into the HGA-2000 graphite furnace.

(3) Hair

Hair samples were washed by a modification of Hammer, et al.(20) method.

All of the hair sample collected (usually 1 to 4 grams) was cut into approximately 1-cm lengths with stainless steel scissors. The hair was placed in a 250-ml Erlenmeyer flask, and a sufficient amount of 0.12% sodium lauryl sulfate solution was added to completely cover the hair. The flask was then placed on a mechanical shaker for 1 hour; then the solution was decanted off, and the hair was rinsed with deionized water until no trace of the surfactant remained. The hair was then washed 2X with isopropyl alcohol and rinsed 3X with deionized water. The washed hair was placed in a polyethylene beaker, covered with thin paper to keep contamination out, and placed in an oven (60°C) until dry.

A 1-g sample of the washed and dried hair was weighed into a Vycor beaker and digested on a hot plate with $HNO_3:HClO_4$ (50:50). The digest was evaporated until dense fumes of perchlorate were given off and was then allowed to cool. The digest was filtered with a glass-fiber filter using 0.1N HNO_3 as rinse. The filtrate was collected in a 10-ml volumetric flask and made to volume with 0.1N HNO_3. This sample was analyzed for Pb by aspirating into an air/acetylene flame.

(4) Feces

A 1.5-g aliquot of homogenized feces was digested with concentrated HNO_3 in a Teflon bomb designed by Rantala and Loring.(21) The bomb was placed on a hot plate at 150°C for 1 hour, removed and allowed to cool to room temperature before attempting to open. The digest was quantitatively rinsed through a glass-fiber filter, and the filtrate was collected in a 10-ml volumetric flask. Deionized water was used to make the volume to 10-ml. This solution was analyzed for Pb by injecting 10-μl aliquots into the HGA-2000 graphite furnace.

(5) Tissues

Tissue samples collected in the baseline study were analyzed for Pb. A 10-15-g portion of the tissue was homogenized with a VirTis "45" homogenizer using stainless steel blades. An aliquot of the homogenate (usually 1-2g) was weighed into a Pyrex ashing boat, placed in a vacuum oven (60°C) overnight, and finally placed in a low temperature asher. The tissue samples were ashed under reduced pressure at 400 watts forward power for 4-8 hours. The remaining ash was then solubilized with 1N HNO_3 and rinsed into a 10-ml volumetric flask. This final 10-ml solution was then used to determine the Pb content of the tissues by aspirating into an air/acetylene flame or injecting aliquots into the graphite furnace.

b. Environmental Samples

(1) Air

Air samples, collected on 20.3- x 25.4-cm glass-fiber filters during the baseline study, were analyzed for Pb (Table 8). A 2.54- x 20.3-cm strip of the filter was cut with stainless steel scissors. The strip was cut into approximately 1-cm squares and placed into a 250-ml Erlenmeyer flask. Two hundred milliliters of 6 N HCl was added, and the sample was shaken for 18-20 hours on a mechanical shaker. The sample was then filtered using a glass-fiber filter that had been prewashed with dilute HCl. The filtrate was collected in a 250-ml volumetric flask and filled to the mark with deionized water. This solution was aspirated into an air-acetylene flame using spiked working standard, made up in the same acid concentration, to quantitate the Pb concentration of the baseline samples.

Verification of this leach method was done by performing a "total digest" of selected air samples and comparing with the results obtained with the leach procedure. The total digest consisted of cutting 2.54- x 20.3-cm strips of the glass-fiber filter and placing into a 500-ml boiling flask, adding 150-200 ml of aqua regia, and refluxing for 16-18 hours. The sample was then filtered and made to 250-ml with deionized water. Analysis of this solution was by aspiration into an air-acetylene flame using spiked working standards, made up at the same acid strength to quantitate the unknown samples. Table 8 shows there is little difference between "leaching" the filters with 6 N HCl and "digesting" with aqua regia.

(2) Soil

Soil samples from the baseline study were analyzed for Pb by a leaching procedure.(22) A 15-20g soil sample was dried in a low (60°C) temperature oven for 48 hours. Then a 5-g sample of the dried soil was weighed into a 125-ml Erlenmeyer flask, and 50 ml

TABLE 8. COMPARISON OF 6N HCl "LEACH" WITH AQUA REGIA "DIGEST" OF GLASS-FIBER AIR FILTER FOR Pb

Sample	6N HCl "Leach"	Aqua Regia "Digest"	% Difference
A1	7.16	7.23	1.0
A2	6.52	7.69	5.2
B1	6.01	6.25	3.8
B2	5.65	5.99	5.7

of leaching solution (3:7 mix of 25% hydroxylamine hydrochloride and 35% acetic acid) was added. The sample was sealed and shaken on a mechanical shaker for 15 hours. The leach solution was filtered through a glass-fiber filter directly into a 2-oz polyethylene sample bottle. Aliquots of the solution were then diluted by an appropriate factor to maintain the Pb concentration within the linear range of the instrument.

(3) Water

Water samples from the baseline study were analyzed for Pb by extracting the ammonium 1-pyrrolidine dithiocarbamate complex of Pb into methyl isobutyl ketone (MIBK).

A 2-ml aliquot of the water was neutralized (pH 7) with NaOH and then buffered with Trisma buffer (pH 7). A 0.1-ml aliquot of 1% APDC solution was added and the sample shaken for 1 minute. Then, 1 ml of MIBK was added and the sample shaken again for 5 minutes. The organic layer was removed and analyzed by injecting 10-µl aliquots into the graphite furnace.

7. Calculations and Analytical Data

a. Instrument Parameters

Table 9 lists the instrument parameters used for analysis of Pb by the flame method.

Table 10 gives the parameters for Pt, Pd and Pb analyses on the HGA-2000 graphite furnace.

TABLE 9. INSTRUMENT PARAMETERS FOR LEAD DETERMINATION BY AIR/ACETYLENE FLAME

Lead Analysis

Spectrophotometer:	
Wavelength	283.3 nm
Source	9 mA
Slit	No. 4 (1.0 mm)
Damping	No. 1
D_2 Arc	ON
Recorder	20 mm/min.
Scale Expand	Auto Conc. with 5 ppm Pb at full scale also 2.5 ppm full scale

Flame:	
Air	30 psi/No. 60
Acetylene	8 psi/No. 40
Aspiration rate	2.5 ml/min.

TABLE 10. INSTRUMENT PARAMETERS FOR THE HGA-2000 DETERMINATION OF Pt, Pd and Pb

Lead Analysis

Spectrophotometer:

Wavelength	283.3 nm
Source	9 mA
Slit	No. 4 (1.0 mm)
Damping	No. 1
D_2 Arc	ON
Recorder	10 mm/min
Scale Expand	1X

Graphite Furnace:

Dry	25 sec at 100°C
Ash	25 sec at 500°C
Atomize	7 sec at 2100°C
Tube	grooved
Gas	N_2 at 20 psi, No. 4 (flow meter), auto interrupt

Platinum Analysis

Spectrophotometer:

Wavelength	265.9 nm
Source	18 mA
Slit	No. 4 (1.0 mm)
Damping	No. 1
D_2 Arc	ON
Recorder	10 mm/min
Scale Expand	3X

Graphite Furnace:

Dry	15 sec at 200°C
Ash	30 sec at 1500°C
Atomize	15 sec at 2700°C
Tube	Regular
Gas	N_2 at 20 psi, No. 4 (flow meter), manual interrupt

Palladium Analysis

Spectrophotometer:

Wavelength	247.6 nm
Source	23 mA
Slit	No. 3 (0.3 mm)
Damping	No. 1
Recorder	10 mm/min
Scale Expand	10X

Graphite Furnace:

Dry	30 sec at 150°C
Ash	30 sec at 1500°C
Atomize	15 sec at 2700°C
Tube	Regular
Gas	N at 20 psi, No. 4 (flow meter), manual interrupt

b. **Standard Solutions**

(1) **Platinum and Palladium**

Quantitation of blood samples for Pt and Pd was accomplished by spiking 15-ml aliquots of whole blood prior to digestion with 50µl and 100µl of a combined aqueous standard containing 1.2 µg/ml Pt and 0.2 µg/ml Pd. These spiked samples represented blood concentrations of: Pt 0.004 µg/ml and 0.008 µg/ml, Pd 0.00067 µg/ml and 0.0013 µg/ml.

Composite samples were spiked according to Table 6, using an aqueous standard containing 2 ppm Pt and 1 ppm Pd.

These spiked samples (blood and composites) were used to quantitate the Pt and Pd concentrations of the unknown samples.

(2) Lead

Pb spikes were added to each type of sample matrix according to Table 11. These spike samples were used to establish an analytical working curve to determine the analyte concentration in the unknown samples.

A series of spike samples were analyzed before and after every 10-20 unknown samples. Both sets of data from the spiked samples were used to construct the analytical working curve used to quantitate the bracketed unknown samples.

TABLE [illegible]. Pb SPIKE LEVELS USED TO CALCULATE ANALYTICAL CURVES

Sample	Quantity of Sample Analyzed	Spike Solution µg/ml	Microliter Volume of Spike Solution Used	Concentration of Pb in Samples
Blood	1 ml	10	0	natural conc.
			5	5 µg/100 ml
			10	10 µg/100 ml
			20	20 µg/100 ml
			30	30 µg/100 ml
Urine	10 ml	10	0	natural conc.
			10	10 µg/l
			20	20 µg/l
			40	40 µg/l
Hair	1 gram	1000	0	natural conc.
			5	5 µg/g
			10	10 µg/g
			25	25 µg/g
Feces	1.5 gram	100	0	natural conc.
			5	0.33 µg/g
			15	1.00 µg/g
			30	2.00 µg/g
			60	4.00 µg/g

c. Analytical Data

(1) Limits of Detection

The limits of detection for Pt, Pd and Pb in the different sample matrices are given in Tables 5 and 7. The limit of detection represents the concentration of analyte which will give a signal-to-noise ratio of 2.

(2) Precision

Ten determinations made on a spiked blood sample gave a Pt concentration of 0.012 μg/ml with a standard deviation of 0.0004 μg/ml (C.V = 3.3%) and a Pd concentration of 0.003 μg/ml with a standard deviation of 0.00012 μg/ml (C.V. = 4.0%).

Lead precision data are listed in Table 12.

(3) Accuracy

Interlaboratory studies are being planned to ascertain the accuracy of these methods by techniques involving analytical methods other than atomic absorption spectrophotometry.

Recovery of added spikes range from 97-101% for Pt and Pd in blood at 0.012 ppm and 0.003 ppm levels, respectively.

Lead recovery of spiked blood (0.2 ppm) range from 96 to 106%, while the recovery range for urine (0.002 ppm) is 89 to 97%. Recoveries of spiked lead in hair (10 ppm) and feces (1 ppm) range from 95 to 103%.

TABLE 12. PRECISION FOR Pb ANALYSIS

Sample	n	Pb Concentration ppm	S.D. ppm	C.V. %
Blood	10	0.178	0.012	6.74
Urine	12	0.01854	0.00292	15.75
Hair	12	26.21	1.799	6.86
Feces	8	0.265	0.184	69.43

8. Special Analysis

a. Paint Analysis for Pb Content

An exterior paint sample from the housing complex, where a majority of the children volunteers in the baseline study lived, was analyzed for Pb.

(1) Analytical Procedure

A weighed amount (0.673 grams) of the paint chips was dissolved in 20 ml of methyl isobutyl ketone. The solvent was then evaporated off using low heat and a flow of N_2. The dried residue was digested with a 1:1 mixture of conc. HNO_3:H_2SO_4 on a hot plate (100°C). The sample was digested for 24 hours, filtered through a glass-fiber filter and the filtrate collected in a 100-ml volumetric flask. Deionized water was used to fill the flask to the mark. A 1:50 dilution of this solution was made prior to aspirating the sample into an air-acetylene flame.

(2) Results

The Pb concentration was 2.4 mg/gram of dried paint. The solubility of the sample in MIBK and the low lead content suggest a latex-type paint.

Ingestion of this type of paint would not be suspected in high blood-Pb levels in children living in the housing complex.

b. Neutron Activation Analysis (NAA)

(1) Blood

The 0.2M TOA (in benzene) extracts from 128 blood samples in the baseline study were composited to make one sample. The 0.02M TOA (in xylene) extracts from 49 blood samples in the mining study were composited to make another sample. These two samples were evaporated to dryness and reconstituted with a known volume of benzene or xylene.

General Activation Analysis, Inc., San Diego, California, did the neutron activation analysis of these sample composites.

(2) Analytical Procedure

The samples plus comparator standards were irradiated for 30 minutes in the TRIGA Mark I Nuclear Reactor at a flux of 1.8 x 10^{12} n/cm^2/sec. After a decay of 24 hours, the samples were wet-ashed under reflux in the presence of palladium and gold carriers. Palladium and gold were then precipitated from the resulting solution, dissolved in aqua regia and counted on a Ge(Li) detector coupled to a multichannel gamma-ray spectrometer. Palladium forms Palladium-109 with a half-life of 13.5 hours, while platinum produces Gold-199 with a half-life fo 3.15 days.

(3) Results

Accounting for the volume of the extracts used for atomic absorption analysis and the volume of TOA recovered from each extract, the Pt and Pd concentration in blood is:

baseline: 4.9 ppb Pt $\leq$ 0.1 ppb Pd

mining: $\leq$ 2.8 ppb Pt $\leq$ 0.38 ppb Pd

The ($\leq$) indicated that no analyte was detected, and the upper limits are based on three standard deviations from the counting statistics.

c. Dilution Tunnel Sweepings

A sample of material collected in the air dilution tunnel of EPA's catalyst dynamometer testing facility was sent to General Activation Analysis, Inc., San Diego, California, for Pt determination by NAA.

(1) Analytical Procedure

The sample was removed from its shipping container and sealed in a tared polyethylene vial. The weight of the sample was 1.0154 grams. A platinum standard was sealed in a similar vial.

Both the sample and standard were irradiated simultaneously for 30 minutes in a TRIGA Mark I Nuclear Reactor at a flux of 1.8×10^{12} n/cm^2/sec. After a twenty-hour decay, the sample vial was opened and the sample placed in a 250-milliliter Erlenmeyer flask. Ten milliliters of gold was added to the sample, and, using the same pipet, 10 milliliters of gold were placed into a third polyethylene vial. This third vial was then heat-sealed.

The sample was wet-ashed with nitric, hydrochloric and sulfuric acids until clear. Gold was precipitated using sulfur dioxide. The metal was washed, dissolved in aqua regia, and the solution placed into a fourth polyethylene vial. This fourth polyethylene vial was then counted for 12 hours on a Ge(Li) detector coupled to a 4096 channel gamma-ray spectrometer. The platinum standard was similarly counted. Platinum produces Gold-199 via the following reactions:

$$\text{Pt-198} \quad (n, \gamma) \quad \text{Pt-199}$$

$$\text{Pt-199} \xrightarrow{\beta} \text{Au-199}$$

Only platinum produces this Gold-199 radioisotope. Gold-199 was detected in the separated sample. It was then quantitated by comparison with the unopened platinum standard.

After the above quantitation, the sealed vial plus the vial containing the 10 ml of gold was placed back in the TRIGA Mark II Nuclear Reactor. After the second irradiation, the two vials were counted as above, and the amount of gold in the sample vial was determined. This procedure determined the recovery factor which, in this case, was 83.6%. The platinum value was corrected for this recovery value.

(2) Results

Sample	Pt (ppm)
Dilution tunnel sweepings CPL, EPA, NERC, RTP 4/75	2.44

d. Vacutainer Contamination Study

(1) Introduction

There has been some evidence[23] that so-called "low-lead" blood collection tubes may actually be contaminated with significant levels of lead. This contamination may be introduced from the manufacturing process, or it may be incorporated into the glass matrix of the tube itself. The evidence from leaching experiments and from microprobe analysis[23] indicates that it is possible both these sources of contamination are responsible for the lead contamination present.

This investigation proposed to look at the lead contamination by a leaching procedure using whole blood, deionized water and a dilute acid (0.1N HCl) as the leaching solutions.

(2) Experimental

(a) Selection of Vacutainers

From previous investigations of lead concentrations in whole blood, the relative standard deviation of the analytical method was known. This allowed the determination of the number of vacutainers that would have to be analyzed to have a preselected confidence interval at the 95% level (see Appendix B). Setting the length of the confidence interval at 0.008 μg/ml would require 40 vacutainers to be analyzed to achieve this interval.

A Hewlett-Packard Model 9810A calculator was used to generate a list of random numbers (random number program). Forty of these random numbers were used to select the vacutainers. Each vacutainer in a case (1,000 vacutainers) was numbered in a systematic fashion, and those vacutainers whose numbers corresponded with the random numbers were taken for analysis.

(b) Analytical Procedure

Instrumental parameters are listed in Table 10.

Lead was selected as the analyte to represent the heavy metal contamination. The lead analysis was based upon the natural level of lead found in whole blood (500cc) purchased from a local blood bank. The method of additions and regression analysis was used to determine the lead concentration in the blood (Figure 7).

Since the program requires data on platinum and palladium concentrations in blood, it was decided that these two metals would also be included in this investigation.

Levels of platinum and palladium in normal (unexposed) human blood have not been determined, but they are so low that to get valid data on these metals from this study it would be necessary to spike the blood (1 ng/ml). Any platinum or palladium contamination from the vacutainers could then be determined by the increased absorption signal. From the design of this investigation, any loss of these metals to the vacutainer surfaces could also be

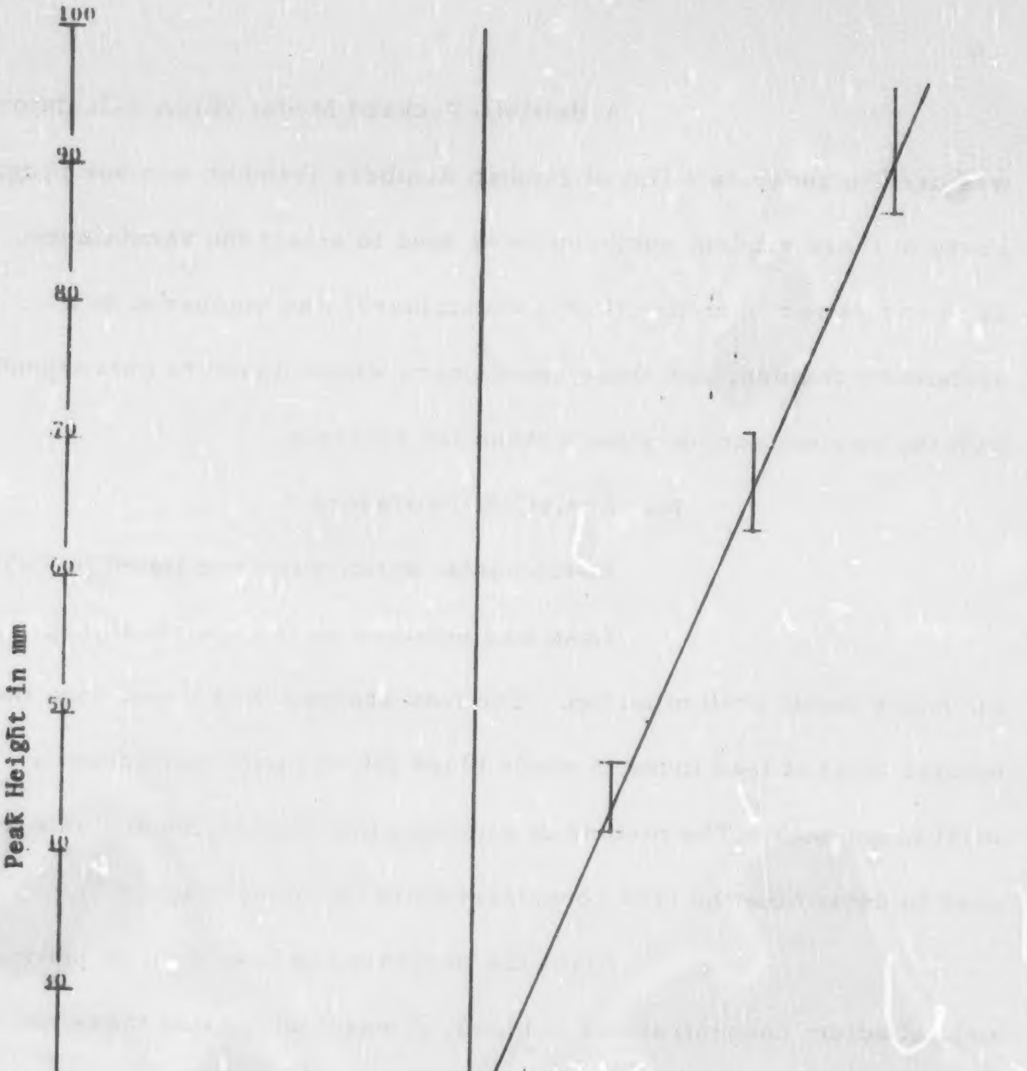


FIGURE 7. REGRESSION ANALYSIS OF BLOOD-Pb SPIKES

determined, provided it was great enough to be above the detection limit of the atomic absorption instrument.

(i) Lead Analysis

The procedure used for lead analysis of whole blood is based upon that of Mitchell, Ryan and Aldous.(18) One milliliter of whole blood is treated with 1.0 ml of a hemolyzing-chelating solution consisting of a non-ionic surfactant (Triton X-100, 5% by volume) and sodium diethyldithiocarbamate (2% by weight). The sample is vigorously shaken and then allowed to stand for 10 to 15 minutes to insure complete hemolysis. One milliliter of methyl isobutyl ketone (MIBK) is added, and the sample is thoroughly mixed and then centrifuged at 3,000 RPM for 5 minutes. The organic layer is removed for lead analysis.

Lead analysis of the water samples followed the same procedure used for blood, but the dilute acid samples were neutralized (pH 7) with 0.1N NaOH prior to extraction.

(ii) Platinum and Palladium Analysis

The extraction of platinum and palladium from whole blood is based upon the methods of Khattak and Magee.(12, 13) Five milliliters of whole blood is digested in a Vycor beaker with $HNO_3:HClO_4$ (70:30) on a hot plate at 200°C. A flow of N_2 is used to evaporate the digest solution to approximately 1 or 2 ml. The remaining digest is reconstituted and evaporated to near dryness twice with concentrated HCl. It is finally reconstituted with 5 ml of 0.1M HCl and quantitatively transferred to a 10-ml volumetric flask. Deionized water is used to fill the flask to the mark. The diluted solution is then placed in an extraction vessel, 1 ml of 25% $SnCl_2$ solution (in 3 N HCl) is added, and the solution is shaken for 30 seconds. Then 0.5 ml (500µl) of a 0.2M tri-n-octylamine solution (in benzene) is added to the extraction vessel and shaken for 1 minute. The organic phase is removed from the vessel and analyzed for platinum and palladium.

(3) Discussion

Whole blood and deionized water were added to the vacutainers by the route commonly used, i.e. with a needle using the vacuum in the tube. The acid leach solution was added by removing the rubber stopper. This prevented the acid solution from being contaminated by the metal needle. Twenty-five of the vacutainers were used for whole blood and the remainder for the deionized water and dilute acid leaches.

All the vacutainers were filled at the same time. Then, at 1-, 3-, 6-, 24- and 30-hour intervals, the blood tubes were analyzed for lead. Vacutainers with deionized water were analyzed for lead at 6-, 24- and 30-hour intervals, and those with dilute acid were analyzed at 6 and 30 hours. Only one analysis was made for platinum and palladium, and that was at 40 hours.

All the vacutainers were maintained at room temperature throughout the study.

At each of the specified time intervals, blood lead analysis was performed on 5 of the blood-containing vacutainers and on 3 control blood aliquots (i.e. blood not exposed to a vacutainer). This gave a direct comparison of the blood-lead levels in the vacutainers, at the specified contact times, with the control bloods, thereby preventing any instrument-parameter variation from affecting the analytical results.

Each vacutainer was sampled for lead only once during the course of this study.

Three deionized water and three dilute acid-containing vacutainers were analyzed at the specified time intervals along with 2 controls (i.e. leaching solution not in a vacutainer) for each.

(4) Calculations

(a) Regression Analysis

Control blood spiked at four different levels was analyzed in duplicate by the extraction method given for lead analysis. Regression analysis was performed on a Hewlett-Packard Model 9810A calculator on the absorption peak heights vs the lead concentrations. The results were that the blood used for this study contained a lead level of 8.47 μg/100 ml ± 0.62 μg/100 ml with a coefficient of variation of 7.3% (see Figure 7).

(b) Statistical Analysis

The data were examined by two different methods (see Table 13). First, the results were calculated on the basis of the

TABLE 13. VACUTAINER STUDY DATA

Time Hours		BLOOD Indiv(a)	BLOOD Mean(b)	WATER Indiv	WATER Mean	ACID Indiv	ACID Mean
1	dif.,mm	3.33	2.96	(no sample)		(no sample)	
	t	1.56	1.31				
	α	0.08	0.10				
	df	16	6				
3	dif.,mm	8.81	8.90	(no sample)		(no sample)	
	t	4.82	5.64				
	α	<0.001	<0.01				
	df	18	6				
6	dif.,mm	5.67	4.81	5.07		4.80	
	t	1.95	1.16	2.97		3.96	
	α	0.035	0.15	0.01		<0.01	
	df	20	6	9		10	
24	dif.,mm	6.24	6.56	1.61	1.61	(no sample)	
	t	1.95	1.99	0.64	0.52		
	α	0.035	0.05	---(c)	---(c)		
	df	17	6	13	3		
30	dif.,mm	7.75	8.03	1.46	2.11	-4.67	
	t	2.87	2.14	0.64	0.90	-0.76	
	α	0.01	0.04	---(c)	---(c)	---(c)	
	df	16	6	10	3	8	

(a) calculations based on number of individual injections of sample aliquot into graphite furnace
(b) calculations based on mean value of each sample analyzed.
(c) α very large

individual sample aliquot injected into the furnace (individual data points). Secondly, the results were calculated on the basis of the mean value of the data points for each sample (mean of data points).

The test to show whether or not there is lead contamination from the vacutainers is a test for the difference between means of independent groups using Student's t distribution. The control bloods (or deionized water or dilute acid leach solutions controls) are labeled group 1, and those from the vacutainers are labeled group 2.

We test the hypothesis:

$$H_o : \mu_1 = \mu_2 \text{ vs } H_a : \mu_2 > \mu_1$$

or whether the mean lead level of the blood in the vacutainers (μ_2) is greater than that in the control blood (μ_1). If we let

$\bar{X}_i$ = the mean of group i

N_i = size of the i^{th} sample

S_i^2 = variance of the i^{th} sample

i = 1,2

the test statistic, t_c, is defined as

$$t_c = \frac{\bar{X}_2 - \bar{X}_1}{\sqrt{\frac{(N_1 - 1)S_1^2 + (N_2 - 1)S_2^2}{N_1 + N_2 - 2}\left[\frac{1}{N_1} + \frac{1}{N_2}\right]}}$$

with $(N_1 + N_2 - 2)$ degrees of freedom (df).

The significance level, $\tilde{\alpha}$, is the probability of obtaining by chance a value as large as t_c from a Student's t distribution with $(N_1 + N_2 - 2)$ degrees of freedom, when the null hypothesis, H_o, is true. Symbolically,

$$P \left[t(N_1 + N_2 - 2) \geq t_c \right] = \tilde{\alpha}$$

If $\tilde{\alpha}$ is less than the chosen significance level (0.05, 0.10, 0.01), then we reject H_o in favor of H_a. If it is greater, we accept H_o as no change in the lead levels.

(5) Results

(a) Lead

(i) Blood

At the 0.05 level, there is no significant difference between the control blood and the vacutainer blood after 1 hour contact time for both the individual peak and mean peak calculations (see Tables 13 and 14). After 6 hours in the vacutainer, the individual peak calculations showed a significant difference between the control blood and the vacutainer blood, but the mean peak calculations for this time interval indicated no significant difference. Since each vacutainer may contain varying amounts of lead but still remain below the limits specified by the manufacturer, and also since the instrument response may not be exactly the same for each individual injection (pipet error, slight variation in graphite tube, etc.), the mean peak calculations

TABLE 14. RESULTS OF VACUTAINER STUDY -- COMPARISON OF CONTROLS AND VACUTAINER BLOOD LEAD

Time Hours	Control Blood µg/100 ml Mean	Control Blood µg/100 ml Std. Dev.	Vacutainer Blood µg/100 ml Mean	Vacutainer Blood µg/100 ml Std. Dev.	Significant Difference at the 0.05 Level (Table 13)
1	8.47	0.28	9.65	1.01	no
3	8.47	0.41	10.25	0.85	yes
6	8.47	1.43	9.76	1.58	?
24	8.47	0.66	9.51	1.22	?
30	8.47	1.20	9.75	0.73	yes

may be a more meaningful indication of the actual lead contamination present. At the 24-hour interval, based upon the mean peak calculations, the difference between control blood and vacutainer blood may or may not be significant. The difference is significant after 30 hours contact time between the blood and the vacutainers.

(ii) Water and Acid

Both the deionized water and dilute acid leaches showed a significant difference between the control leach solution and that in the vacutainers after 6 hours (see Table 13). At the 24- and 30-hour intervals, there were no significant differences between the controls and the vacutainers for each the dionized water or dilute acid leaches.

(b) Platinum and Palladium

There was no indication of contamination of the vacutainers with these metals. After 40 hours, there was a significant difference between the spiked controls and the vacutainers spiked blood levels (see Table 15), but this difference indicated a "loss" of the platinum and palladium spike to the container.

(6) Conclusion

(a) Lead

The lead contamination found in this particular case of B-D vacutainer 10-ml tubes is approximately 0. 13 µg per tube (see Table 14). This is within the 0. 1 µg per tube level specified by the manufacturer's certification.

TABLE 15. VACUTAINER STUDY Pt and Pd RESULTS

	Platinum		Palladium	
	Control mm	Vacutainer mm	Control mm	Vacutainer mm
	13	12	62	56
	8	7	54	56
	8	8	67	53
	11	5	69	
	5	11		
Mean	11	8.6	63	55
Std. Dev.	3.1	2.9	6.7	1.7
t (0.05)	2.53		3.39	
df	8		5	
Significant	yes		yes	
% diff (means)	22		13	

The fact that the lead level remains relatively constant with regard to exposure time would indicate that it is not tightly bound to the glass matrix of the vacutainer. Also, the lead contamination does appear to be uniformly constant throughout a given lot of vacutainers but within the stated limit.

(b) Platinum and Palladium

There was no evidence that the vacutainers contained detectable amounts of either platinum or palladium. The data do indicate that after exposing spiked blood to the vacutainers for 40 hours there is a 22% "loss" of the platinum spike and 13% "loss" of the palladium spike.

(c) Contamination

There should be no problem with contamination when using these vacutainers for peidemiological invertigations. The only precuation that should be followed is to remove the blood from the vacutainer and place it in a linear polyethylene container (acid washed) within a few hours after it has been drawn. This would prevent "loss" of the analyte metals to the walls of the vacutainers.

e. Lead-210 Study

(1) Selection of Subcontractor

Five firms were contacted to see if they were interested in performing ^{210}Pb analysis on a limited number of biological and environmental samples. Two of the companies were not set up to perform ^{210}Pb determinations on a routine basis and were not interested in doing the limited number of samples. Another company was interested but did not have the necessary standards available. A fourth company said they could find no reasonable method to determine ^{210}Pb utilizing either fast or thermal neutron activation analysis. The LFE Environmental Analysis Laboratories, Richmond, California, was interested and sent a price quote for ^{210}Pb analysis. This company was selected to perform the analysis.

(2) Method of Analysis

(a) Sample Preparation

(i) Blood and feces samples from the baseline survey were removed from the freezer and packed in a styrofoam mailing carton with enough dry ice to last 72 hours. The blood samples were sealed in a polyethylene bag to protect them from the feces samples. A total of 30 blood samples (in 30-ml polyethylene bottles) and 30 feces samples (in 60-oz polyethylene jars) were shipped by air express for ^{210}Pb analysis.

Three glass-fiber air filters used to collect particulate matter in the baseline survey were sealed in individual polyethylene bags. The bags were then sealed in an insulated envelope for air shipment with the other environmental samples.

Eight soil samples (16-oz polyethylene jars) were packed in an insulated mailing carton with enough dry ice to last 72 hours. This carton was shipped by air express for ^{210}Pb analysis.

(ii) The soil and feces samples were dried at 110°C to constant weight and the dry weight of the sample recorded. The samples were then ashed at 450°C to remove any carbonaceous and/or organic materials.

(b) Sample Dissolution

The air filters and ashed feces and soil samples were dissolved with successive HNO_3-HF treatments to achieve complete dissoltuion. The dissolved sample was equilibrated with standardized Pb carrier. The total blood sample was wet ashed with HNO_3 in the presence of standardized Pb carrier.

(c) Decontamination

The equilibrated samples were purified radiochemically by precipitating a lead carbonate, lead iodide, and a lead nitrate. For the soil samples with high concentrations of Fe, the Fe was removed with a Hexone extraction. The purified ^{210}Pb was mounted as lead sulfate, and the radiochemical yield was determined by weighing the lead sulfate and by correcting for the macro Pb in the sample. The time of the lead sulfate precipitation is recorded as the final separation time of ^{210}Pb-^{210}Bi.

(d) Counting

The lead sulfate contained in a Mylar sandwich on a plastic planchet is counted on a CE-14 low background beta counter as soon as possible after the ^{210}Pb-^{210}Bi separation time. The sample is counted five times within a period of two weeks to observe the ^{210}Bi ingrowth.

(ii) The soil and feces samples were dried at 110°C to constant weight and the dry weight of the sample recorded. The samples were then ashed at 450°C to remove any carbonaceous and/or organic materials.

(b) Sample Dissolution

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(d) Counting

The lead sulfate contained in a Mylar sandwich on a plastic planchet is counted on a CE-14 low background beta counter as soon as possible after the ^{210}Pb-^{210}Bi separation time. The sample is counted five times within a period of two weeks to observe the ^{210}Bi ingrowth.

(e) Calculations

The standard method for ^{210}Pb analysis at LFE involves a separation of the daughter ^{210}Bi and multiple beta counts of the sample as the ^{210}Bi grows back into equilibrium. The counting is done on a CE-14 low background beta counter. Sixteen of these counters are on-line at LFE with backgrounds of 0.4 to 0.5 cpm. The sample is counted through a thin aluminum absorber (4.75 mg Al/cm^2) to screen out any ^{210}Po alpha particles. The ^{210}Pb beta particles (0.061 MeV maximum) do not register on the counters. All counts are assumed due to ^{210}Bi (1.160 MeV maximum).

Punched data cards are produced for each measurement on the sample by the computer. All sample information is available in disk files, and on a routine basis, no keypunching is required.

The calculation is done by computer. A weighted linear least squares analysis is performed on the growth data resolving an equilibrium ^{210}Bi value and an assumed long-lived component. All data points are corrected for growth during counting and are weighted as the inverse variance of the net cpm as derived from counting statistics. After an initial fit, points that are more than 2σ (counting statistics) away from the fitted value are rejected and a second fit is done. Errors are computed by propagating errors due to counting statistics through the least squares formula. If the data points do not fit the determined line as well as would be expected from the counting statistics, a larger error, based on the goodness of fit, is used.

(3) Limit of Detection in Blood and Feces

(a) Blood - On a 10ml blood sample, the limit of detection for ^{210}Pb is 0.045p Ci/total sample.

(b) Feces

A 10-g (dry wt.) sample has a detection limit of 0.05 μ Ci/gram for ^{210}Pb.

9. Discussion and Conclusions

a. Platinum and Palladium

An extraction system designed to handle a large number of samples on a routine basis must keep procedural steps to a minimum.

The HMWA extraction system described here is a relatively simple means to extend the limit of detection of the atomic absorption analysis of Pt and Pd.

Further improvements in this HMWA extraction system could improve the abosolute amount of Pt and Pd which may be determined. The excessive amount of "smoke" during the atomization of the extract limits the volume of TOA which may be injected into the graphite furnace. Decreasing the concentration of TOA has been only partially successful in eliminating this problem. Increasing the ashing temperature has not helped either. There are losses of analyte at the temperature needed to remove the excess matrix.

This excessive "smoke" during atomization necessitates that the hollow cathode lamp and the deuterium arc lamp (background corrector) be alined very carefully, or incorrect absorption readings will result. Pd is affected more by incorrect alinement than is Pt.

Composite samples were another means of increasing the limit of detection for Pt and Pd. Experience in this laboratory has shown that wet ashing large quantities of solid material requires an excessive amount of time. Digestion of spiked composite hair and feces samples gave very erratic results. Recoveries were in the range 30-70% for Pt and Pd in feces and hair.

Spiked urine composite recoveries for Pd ranged from 0-60%, and for Pt the range was 0-100%. More work needs to be invested in this area to make it a reliable method for increasing the sensitivity of Pt and Pd determinations.

The limits of detection given in Table 5 for urine, hair and feces are calculated on the basis of complete (> 90%) recovery using the extraction procedure outlined. The limit of detection for blood is calculated on the basis that the absolute limit of detection for our instrument is Pt = 1.07 ng and Pd = 0.33 ng.

Analysis of particulate matter collected on glass-fiber filters for Pt and Pd is limited by the total amount of material on the filter. Samples collected in the mining study contained such large amounts of particulate matter that large volumes of acid were needed to solubilize all the analytes present. Removal of this acid required an excessive amount of time.

Extracts of the air samples collected in the mining study contained an interference which prevented their analysis. This interference was thought to be very fine particulate matter which was not digested or removed by filtering and was subsequently trapped in the TOA extract. Background correction could not compensate for this interference.

Another set of air samples collected at the mining study site contained less particulate matter. Analysis of these filters by the method described was possible.

The extraction of Pt and Pd in a single extract using a liquid anion exchanger (tri-n-octylamine) from an approximately 3N HCl solution provides a means of concentrating these elements so they will be within the detection limit of AAS using the flameless graphite furnace. The procedure improves the limit of detection for Pt and Pd in biological samples and also provides a means of improving the sensitivity of AAS analysis for Pt and Pd.

b. Lead

The extraction procedure for blood Pb provides a simple and fast means of analyzing a large number of samples. Table 12 shows that the method has good precision.

Table 11 gives the quantity of spike solution added to 1 ml of blood to determine the analytical regression curve (Figure 7) used to calculate the unknown blood samples. Attempts at spiking a large quantity of blood at different levels of Pb concentration and then using an aliquot for analysis have produced erratic results in our laboratory. The spike is added directly to the sample prior to extraction.

The limit of detection for Pb in blood is restricted more by the reagent blank signal than by the background noise level of the instrument. Attempts to remove Pb from the reagents has been only partly successful.

Extraction of urine Pb by this procedure gives a rather high C.V. (Table 12). One reason for this is the low concentration of Pb normally found in urine. Another reason may be that the 1% acetic acid used in this laboratory to preserve the urine samples is not sufficient to maintain all the urine components in solution.

Like blood, the limit of detection of Pb in urine is a function of the reagent blank's Pb concentration. High reagent blank absorption increases the limit of detection. Urine samples are spiked similarly to the method given for blood (Table 11) and for the same reason.

Hair analysis for Pb by the air-acetylene flame provides good precision (Table 12). The most common reason for coefficients of variation greater than 7% is improperly washed hair.

The limit of detection for Pb in hair by the flame method is limited by the instrument noise level rather than reagent blank interference. Spikes are added to the hair samples right after the digestion acid has been added.

Feces analysis for Pb varies (Table 12) because it is difficult to obtain a completely homogeneous sample. Even though the samples are homogenized prior to analysis, the relatively small sample analyzed (1.5 grams) makes it difficult to imrpove upon the analytical variation.

Digestion of the feces in the Teflon bombs is a fast and easy method to analyze for Pb. The limit of detection is restricted by the Pb concentration in the reagent blank and the size of sample which may be used. Use of suprapure acids has decreased the reagent blank absorption but has not completely eliminated it.

Determination of Pb in fecal samples by "closed" digestion is considerably faster than "open" digestion methods, but precision suffers because of the nonhomogenity of the sample.

The procedures for Pb analysis in blood, urine, and hair provide fast and reliable methods of determining Pb in these commonly used epidemiological monitors of environmental health.

Leaching of air filters and soil samples with acids is a better method to determine Pb in these sample matrices rather than lengthy "total" digestion procedures commonly used. Care must be taken to verify that all the analyte is being removed using the leach procedure.

E. Data Processing

Two types of data forms were processed on this project. A questionnaire form providing personal information pertinent to this study was completed by each person volunteering as a human subject participant for the human subject sampling. A metal analysis form for coding chemical analysis results was completed for each sample analyzed in the laboratory.

The questionnaire was filled out by prospective study participants. The Los Angeles, Lancaster, and Ontario particiipants completed the Platinum, Palladium and Lead Questionnaire, OMB-158-S-74010, while the New Jersey participants completed a brief Information Form. Upon their receipt, the questionnaires for a study site were coded, assigned an ID number, keypunched, and listed in name, sex, and age sequences for selection of the most appropriate participants. The Principal Investigator and the Project Officer selected the study participants to meet the planned age and sex distributions at each baseline site.

To insure accurate reporting, transmission, and interpretation of the analytical determinations on each collected sample, a fifteen-character label code was devised for this project and similar epidemiological studies. The code consisted of four characters identifying the project, two characters identifying the site, three characters for the sampling period and subperiod or sample number, one character specifying the sample medium, and one character for the analysis to be performed, and four characters giving the ID number for a human subject or the location identification for an environmental sample. Documentation of the label code is shown in Appendix D.

A label generation computer program was developed to print up the required number and types of sample labels for each container into which the human subject and environmental samples were to be placed during sample collection and processing. The fifteen-character label code, the sample medium (blood, feces, air, water, etc.), and the sampling period or sample number were printed on each sample label. On the human subject sample labels, the participant's name was printed on the labels to be used for sample collection, but it was deleted from the processing sample labels. Two samples of the sample labels are shown below.

```
                        URINE
2222UMLA1133881      FIRST SAMPLE


                        BLOOD
2278BMLA1233881     SECOND SAMPLE
```

When the study participants at a site had been selected, their keypunched questionnaire cards and instructions regarding the type and number of labels were input into the label generation computer program. All of the sample labels needed for collection and processing of the site's samples were printed by the program in a sequence that would facilitate their use.

Later, when the chemical analysis of a set of samples from a site was completed, the results were reported for data processing and statistical evaluation on the Metal Analysis Coding Form. This form was specifically designed for transmitting the chemical determinations obtained on this project and related epidemiological studies. For each sample analyzed, the fifteen-character sample label code, the sample medium, and each of the analytical determinations (metal, concentration, and units) were recorded on the Metal Analysis Coding Form. A reduced copy of the form is presented in Appendix D. The information on each set of Metal Analysis Coding Forms was checked and then keypunched.

After all the human subject sample determinations were received and keypunched, the questionnaire data cards and the metal analysis determination cards for each type of sample were merged into a single file that was sorted by ID number and card type. A computer program was written to abstract the necessary questionnaire and sample determination information from the file in a form suitable for statistical analysis.

The data processing of the environmental samples was done manually. This was because there were few air, soil, and water samples with positive chemical determination, and because various sampling configurations were used.

F. Statistical Methods

1. Baseline

a. Environment

The statistical methodology was to characterize and compare the environments of the Los Angeles and Lancaster human subject participants. Because there were no detectable levels of platinum or palladium in any of the individual baseline environmental samples, only the detected lead concentrations were statistically analyzed.

Two air samples were obtained at the Los Angeles participants' residence, the U. C. L. A. married student apartment, for lead analysis. Thirteen air samples were obtained from the backyards of some of the Lancaster participants. The lead concentration determinatio of these Los Angeles and Lancaster air samples were compared. The standard t test of two independent samples was used to detect any significant difference in the mean air lead concentration. The t test assumes both sampled populations are normally distributed with equal variances. The equality of variance assumption for the two independent comparable groups was tested by the standard F-test. The validity of these assumption was examined for each set of tissue data without transformation, under logarithmic transformation, and under square root transformation. The square root transformation yielded acceptable variance equality between the two air quality populations, whereas the logarithmic and untransformed data did not. Hence, a two-sided t test was applied to the square root transformed lead determinations for each air sample.

The soil lead analysis focused on characterizing the relationship between the surface soil lead concentration and the distance upwind or downwind from the freeway in Los Angeles. Graphical techniques were used to present the soil lead results from two Los Angeles locations adjacent to the San Diego Freeway as a function of the upwind and downwind distance. The configuration of the Los Angeles soil sampling permitted only one soil lead sample to be taken at the Los Angeles participant's residence. Seven soil samples were obtained from the backyards of Lancaster participants and analyzed for their lead concentration. Dixon's gap test(24) for outliers was used to determine whether the Los Angeles residence soil sample could be considered a member of the Lancaster soil population. Inspection indicated that the logarithmically transformed Lancaster soil data appeared more normally distributed data than either the untransformed or square root transformed data. In addition, use of logarithmically transformed data would yield the most conservative Dixon test (i.e., considering the Los Angeles sample as an outlier only when it certainly must be an outlier). For these reasons, the Dixon gap test was applied to the logarithmically transformed soil lead data.

Five samples of tap water were obtained from the homes of Los Angeles and Lancaster participants and analyzed for their lead concentrations. The two-sample t test was used to test the null hypothesis of no difference in the mean lead concentration of the Los Angeles and Lancaster water supplies. Since square root transformed data yielded acceptable equality of variance, the two-sided t test was conducted on the square root transformed data.

b. Human Subjects

The statistical analysis methodology was to compare the mean platinum, palladium, and lead concentrations in the blood, long and short hair, urine, and feces samples from corresponding groups of 137 participants from the Los Angeles site and 125 participants from the Lancaster area. Because none of the participant samples had detectable platinum or palladium concentrations, the statistical analysis was restricted to the lead concentration data. The two blood, urine, and feces samples obtained during the week from each participant were considered replicates; their mean was utilized as the observed participant value. When a reported lead concentration was below the analytical method's detection limit, the detection limit was substituted as the concentration in the statistical analysis.

Three Lancaster participants had extremely high outlier hair lead values. A retired man had a lead concentration of 4,700 μg/g in his long hair sample. An elderly lady's hair samples showed lead levels of 3,800 μg/g in the long hair and 760 μg/g in the short hair. A preschool

girl who lived with the elderly lady had hair lead levels of 130 µg/g in her long hair and 940 µg/g in her short hair. Since the three were neighbors in an isolated area who all spent the entire day at home and who all had normal blood and urine lead levels, a non-vehicular lead source was hypothesized. Thus, the hair lead data on these three participants was excluded from the statistical analysis.

The standard t test of two independent samples was utilized to compare corresponding participant groups from the two sites with respect to significant differences in population means. Site comparisons were conducted for each tissue on the total participant groups and on subgroups stratified by sex and age. The t test assumes both sampled populations are normally distributed with equal variances. The normality assumption was examined by testing the skewness of the group observations.(25) The equality of variance assumption for the two independent comparable groups was tested by the standard F-test. The validity of these assumptions was examined for each set of tissue data without transformation, under logarithmic transformation, and under square root transformation for the total group and the male and female subgroup comparisons across site. In every case, the logarithmic transformation yielded the more valid t tests. Thus, logarithmically transformed lead concentration data was utilized. Each t statistic tested the null hypothesis of equal population or stratum means across site against the two-sided alternative of unequal means.

The lead concentrations of the blood, hair, urine, and feces samples from the participants at the two sites were also related to various potentially pertinent factors in addition to sex and age. These additional factors were preschool-nursery vs children in school, length of residence in the city, distance from the expressway, distance from other highways, types of air conditioning, level of cigarette smoking, ethnic grouping, and occupation. Because these additional factors were not considered in the participant selection process, most of these factors were highly correlated with the site. For example, 85% of the Los Angeles participants had no air conditioning, while 55% of the Lancaster participants had central air conditioning and another 18% had window units. Because of the design interactions of these additional factors with the site, each factor was analyzed both as a main effect and within site in relation to the lead concentration data for each tissue. The effects of each factor were inspected using both the original and logarithmically transformed data. All the detected main effects proved to be spurious; actual site and/or age effects, masquerading through the design interaction as the effect of an additional factor, were responsible for the apparent factor effect. Only when an additional factor showed a consistent relationship to the lead determinations for two or more tissues at the same site was the apparent factor effect subjected to a formal t test of significance. When the factor had more than two levels, the nature of the relationship of the factor to the lead mean determined the definition of the two groups submitted to the t test. When the factor possessed level ordering and the lead mean varied according to this ordering, the lowest and highest levels of the factor were taken as the compared groups. Otherwise, all the levels of the factor were compressed into the two best comparison groups. The null hypothesis of equal lead concentration means was compared against the alternative of an elevated mean for the logically affected group using a one-sided t test. The data were logarithmically transformed prior to each t test to better satisfy the equality of variance assumption.

Two blood, urine, and feces samples were obtained on consecutive days from most of the Los Angeles and Lancaster participants. For all the lead determinations made on a given tissue from a given site-sex-age group, the between participant variation was compared against the within participant variation. The between participant variance measures the amount of lead determination variability from one participant to another in the given tissue and site-sex-age group. The within participant variance measures the lead determination variability between the two samples from each participant in the group. The null hypothesis that the between participant variance equals the within participant variance was tested against the alternative that it exceeds the within participant variance using a variance ratio F test.

In many cases, the F test accepted the null hypothesis. The implication in such cases is that the two samples obtained on consecutive days from a single person have as much lead variability as two samples taken from different people in the same site-sex-age group. To further examine this sampling variability and to determine whether the analytical method was the responsible factor, an additional blood sampling experiment was performed. Sixteen blood samples were taken from an adult male at the same time. Each sample was separated into two aliquots. Each aliquot was processed, frozen, and analyzed for lead using the same procedures employed with the Lancaster and Los Angeles participant blood samples. An analysis of variance was conducted using the logarithmically transformed lead determinations to examine the variation between samples and between aliquots within a sample. The interaction term was used to estimate the precision variance of the combined processing/analytical procedure. The variance components estimated from this sampling experiment were compared against the participant and sampling variability obtained with the comparable group of Lancaster and Los Angeles participants (males aged 17-34) to evaluate the sources of variation.

2. Refineries

a. Environment

The environment of New Jersey refinery workers was examined through 24-hour ambient air samples obtained for five consecutive work days in both the refinery and salts sections of the refinery. The platinum and palladium concentrations of each sample were determined. The statistical methodology was to characterize the distribution of platinum and palladium in the air in the refinery and salts sections. Characterization consisted of tabulating the concentration determinations by work section and calculating the mean and standard deviation of each set of data.

A relatively high palladium determination was obtained on the Monday air sample in the refinery section. Since even with dilution this sample was above the linear calibration range for palladium, its value was estimated as 0.356 $\mu g/m^3$. It is uncertain whether this sample represents a valid palladium concentration resulting from an operational malfunction in the refinery section or whether the sample was contaminated. For this reason, the palladium characterization of the refinery section air was presented both including and excluding the Monday sample. It should be noted that the workers urine specimens were collected Monday night and Tuesday morning and that the blood samples were taken on Tuesday. Hence, if there was a very high palladium air concentration in the refinery section on Monday, it could have had an effect on the palladium results from the New Jersey participants.

b. Study Participants

Single samples of blood and urine were obtained from each of 61 refinery worker participants. The platinum and palladium concentrations of every blood sample were below the analytical method's detection limits. However, of the 58 urine samples obtained and analyzed, 6 had platinum concentrations above the platinum detection limit of

1.4 µg/l, and 34 had palladium concentrations above the 0.4 µg/l detection limit for palladium. Because the detectable platinum determinations were few and isolated, the sample results were simply reported without any statistical analysis.

The palladium determinations from the New Jersey workers were subjected to an appropriate statistical analysis. Each palladium determination below the analytical detection limit was set to the limit for the statistical analysis. The original data and their logarithmic transformations were examined. The logarithmic transformation yielded the more normally distributed data; it was used for the subsequent analyses. The mean and standard deviation were used to characterize the palladium distribution, both for all the workers and for the workers in each of the five work sections. A one-way analysis of variance by work section was conducted to test whether the mean urine palladium level was the same for the workers in each work section.

Correlation analysis was used in attempting to relate the ln(Pd) urine determinations to each of six potentially relevant factors: age, race, cigarette smoking, length of employment, work section, and work shift. The work sections were ordered from highest to lowest anticipated palladium exposure: refinery (1), salts (2), recovery (3), maintenance (4), and storeroom (5). For each factor, the null hypothesis of zero correlation was tested against the two-sided alternative using the statistic $r\sqrt{n-2}/\sqrt{(1-r^2)}$ which has the t distribution with n-2 degrees, where n is the number of pairs on which the correlation coefficient r was computed. R. A. Fisher demonstrated that for this test of zero correlation, it is sufficient that only one of the variates be normally distributed.(26) The correlation analysis was conducted for two situations: using all 58 palladium determinations with negative results valued at the detection limit, and using only the 34 palladium determinations exceeding the detection limit.

V. RESULTS

A. Baseline

1. Platinum and Palladium

Data for platinum and palladium in study participants of Los Angeles and Lancaster are shown in Table 16. No detectable levels were found in individual samples; thus, "less than" values (detection limits) are shown. In an effort to obtain some idea of the actual levels present in blood, a composite of blood from all age groups and both sexes of Los Angeles and from Lancaster was analyzed for platinum and palladium. Measureable levels were found for platinum as seen at the bottom of Table 16.

Autopsy samples were collected in Los Angeles from a pathologist at a teaching hospital. Table 17 shows the information obtained for these autopsy cases. For each autopsy, samples of liver, kidney, spleen, lung, muscle and fat were collected. No detectable levels of these two metals were found in these tissues. Table 18 shows the "less than" values for each of these tissues.

Platinum and palladium were also measured in ambient air, soil and tap water samples collected in Los Angeles and Lancaster. No detectable levels were found at the following detection limits:

	Platinum	Palladium
Ambient air	$<5 \times 10^{-8}$ µg/m^3	$<6 \times 10^{-8}$ µg/m^3
Tap water	<0.08 ppb	<0.024 ppb
Soil	<0.8 ppb	<0.7 ppb

TABLE 16. PLATINUM AND PALLADIUM LEVELS IN SOUTHERN CALIFORNIA

	Los Angeles and Lancaster							
	Blood-μg/100 ml		Urine-μg/liter		Hair-μg/g		Feces-μg/g	
Age Group	Pt	Pd	Pt	Pd	Pt	Pd	Pt	Pd
I	<3.1	<0.9	<0.6	<0.3	<0.05	<0.02	<0.002	<0.001
II	<3.1	<0.9	<0.6	<0.3	<0.05	<0.02	<0.002	<0.001
III	<3.1	<0.9	<0.6	<0.3	<0.05	<0.02	<0.002	<0.001

	Composite Blood Sample μg/100 ml			
	Los Angeles		Lancaster	
	Pt	Pd	Pt	Pd
All Age Groups	0.049	<0.01	0.180	<0.1

TABLE 17. AUTOPSY CASES - LOS ANGELES

Sample I. D.	Age	Sex	Smoking History	Cause of Death
A 7572	64	M	No	Pancreatic CA
A 7593	44	M	Yes	Cardiac arrest
A 7617	69	M	Unknown	Carcinoma larnyx
A 7653	12	M	No	Aplastic anemia
A 7657	74	M	Yes	Carcinoma urinary bladder
A 7561	67	F	Yes	Acute lymphacytic leukemia
A 7587	41	F	Unknown	Adenocarcinoma cervix
A 7621	79	F	Unknown	Hypotension/hypoproteinemia sepsi
A 7654	65	F	Yes	Myocardial infraction
A 7658	47	F	No	Hypertensae cerebrovascular accident

TABLE 18. PLATINUM AND PALLADIUM IN AUTOPSY SAMPLES - LOS ANGELES

	Pt ppb	Pd ppb
Liver	< 0.24	< 0.6
Kidney	< 2.6	< 6.7
Spleen	< 1.3	< 3.3
Lung	< 1.3	< 3.3
Muscle	< 0.9	< 2.2
Fat	< 1.3	< 1.6

These results indicate that baseline levels of platinum and palladium in environmental samples and in human populations in the Southern California area are extremely low. The levels in all instances, other than composite samples, are below the detection limits of atomic absorption.

2. Lead

a. Environment

The air lead determinations made from the samples collected 80 feet downwind from the freeway in Los Angeles and outside the residences of the Lancaster participants are presented in Table 19. The statistical analysis of these air lead data is presented in Table 20. The square root transformed data was used in conducting the t test, because it gave acceptable variance equality for the Los Angeles and Lancaster sites. The t test shows that the average lead concentration in the air approximately 80 feet downwind from the San Diego Freeway in Los Angeles was very significantly greater than that in the air in the backyards of the Lancaster participants.

The configuration and lead determinations of the soil samples taken near the San Diego Freeway in Los Angeles are shown in Figure 8. These lead determinations are plotted in Figure 9 as a function of the distance in the prevailing upwind and downwind directions from the San Diego Freeway at the two Los Angeles soil sampling locations. Figure 9 illustrates the general agreement of the soil lead

Table 19. Baseline Air Lead Sample Data

	Air Lead Concentration, $\mu g/m^3$	
	Los Angeles Site	Lancaster Site
	6.84	0.40
	5.83	0.83
		0.60
		0.51
		0.44
		0.41
		0.64
		0.58
		0.48
		0.87
		1.03
		0.90
		0.69
Number of samples	2	13
Mean	6.34	0.64
Standard Deviation	0.71	0.21

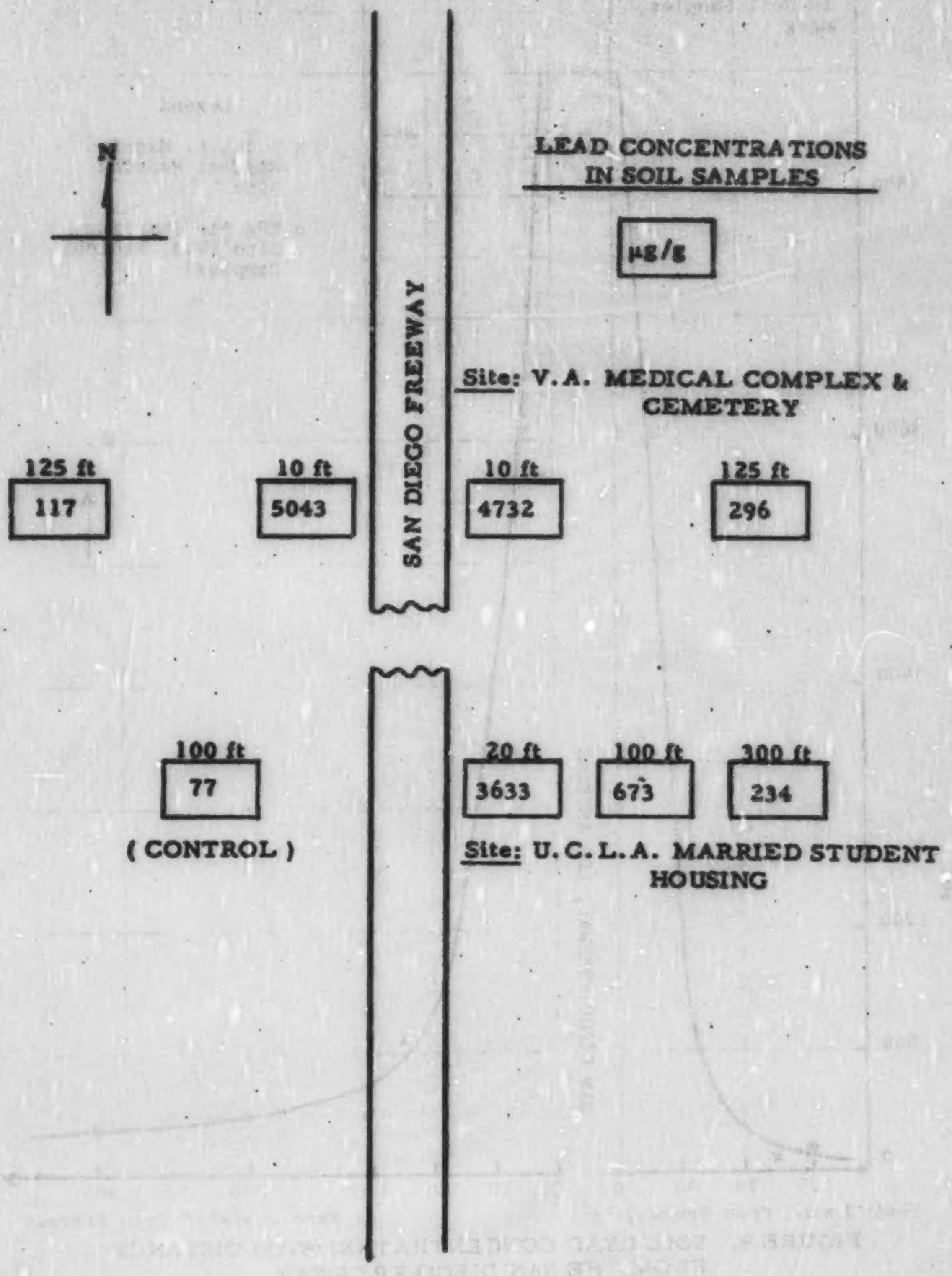
TABLE 20.

COMPARATIVE ANALYSIS OF BASELINE AIR LEAD DATA

	Data Transformations		
	None	**Square Root**	**Natural Log**
Means			
Los Angeles	6.34	2.516	1.843
Lancaster	0.64	0.794	-0.484
Variances			
Los Angeles	0.510	0.0155	0.0128
Lancaster	0.042	0.0159	0.1000
Equality of Variance			
F Test Statistic	12.03	1.024	7.81
Variance equality	No, P=.005	Yes	No, P=.02
Equality of Means			
t Test Statistic		18.00	
P value		$P \ll .001$	

FIGURE 8.

BASELINE SOIL LEAD SAMPLE DATA


N
LEAD CONCENTRATIONS IN SOIL SAMPLES
µg/g
SAN DIEGO FREEWAY
Site: V.A. MEDICAL COMPLEX & CEMETERY
125 ft
117
10 ft
5043
10 ft
4732
125 ft
296
100 ft
77
(CONTROL)
20 ft
3633
100 ft
673
300 ft
234
Site: U.C.L.A. MARRIED STUDENT HOUSING

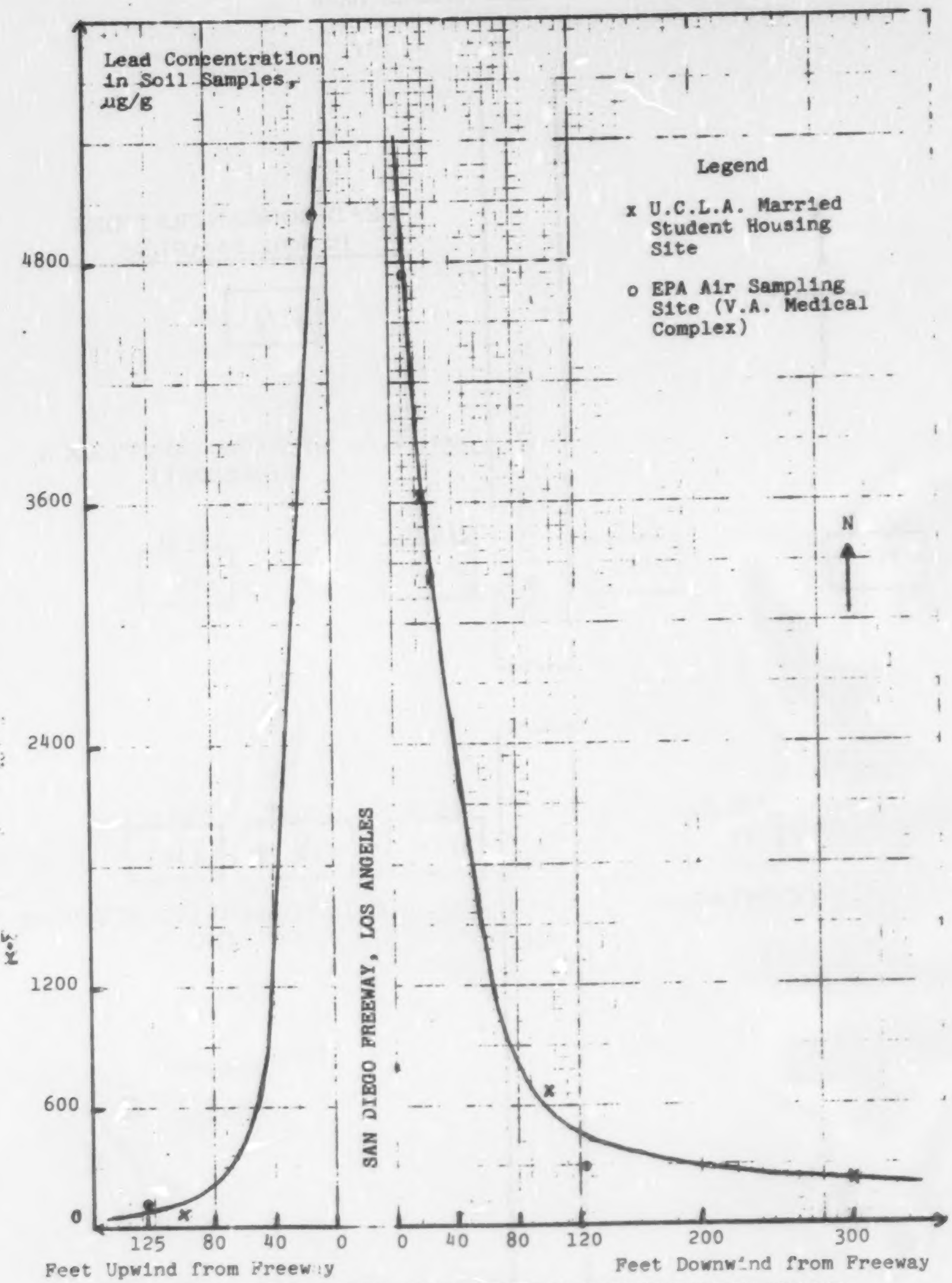


FIGURE 9. SOIL LEAD CONCENTRATION WITH DISTANCE FROM THE SAN DIEGO FREEWAY

data from the two Los Angeles sampling sites adjacent to the San Diego Freeway with respect to distance downwind or upwind from the expressway. Within ten feet of the expressway, the air turbulence created by the vehicular traffic flow apparently distributes the emitted lead equally on both the upwind and downwind sides of the expressway. However, the rate of reduction of soil lead concentration is much more gradual on the prevailing downwind side of the expressway. For example, at a distance of 100 to 125 feet from the expressway, the downwind soil lead concentration is from 3 to 9 times higher than the upwind soil lead concentration.

The soil lead determination obtained at the Los Angeles participants residence, the U.C.L.A. married student apartments, is compared against the seven Lancaster soil lead determinations in Table 21. The logarithmic transformation of the soil lead determinations is chosen for conducting the Dixon gap test of the potential Los Angeles outlier, because it best satisfies the normality assumption of the Dixon test and because it yields the most conservative test. The Dixon test indicates the Los Angeles sample definitely is an outlier from the Lancaster soil sample population. Thus, the soil lead concentration at the Los Angeles participants' apartment complex was significantly greater than the soil lead concentration in the Lancaster participants' backyards.

The lead concentrations were determined for five samples of tap water obtained both from the Los Angeles participants'

TABLE 21.

OUTLIER ANALYSIS OF BASELINE SOIL LEAD DATA

		Data Transformations		
		None	**Square Root**	**Natural Log**
		µg/g		
Lancaster Samples	1	54	7.35	3.99
	2	43	6.56	3.76
	3	49	7.00	3.89
	4	79	8.89	4.37
	5	62	7.87	4.13
	6	83	9.11	4.42
	7	98	9.90	4.58
Lancaster Mean		66.9	8.09	4.16
Lancaster Standard Deviation		20.2	1.23	0.30
Los Angeles Sample		3633	60.27	8.20
Combined Site Statistics:				
Mean				4.67
Standard Deviation				1.45
Dixon gap test statistic				0.815
Outlier				Yes, $P < .001$

apartments and from the Lancaster participants' homes. The lead data and its statistical analysis are presented in Table 22. There was no significant difference between the mean lead concentrations of the tap water supplied to the Los Angeles and Lancaster participants.

The building surfaces of the U.C.L.A. married student housing facility were examined for lead, and the values were less than 3.0 mg/g of dried paint.

b. Study Participants

The standard t test of two independent samples was utilized to compare corresponding participant groups from the two sites with respect to significant differences in population means. Site comparisons were conducted for each tissue on the total participant groups and on subgroups stratified by sex and age. The t test assumes both sampled populations are normally distributed with equal variances.

The normality assumption was examined by testing the skewness of the group observations. The skewness test was applied to the data and its square root and logarithmic transformations to determine which transformation produced the least skewed data (i.e., the transformation under which the normal distribution assumption was best justified). Table 23 displays the results of the skewness tests by P value. The smaller the P value, the less justified is the normal distribution assumption. P values above 0.05 are interpreted as accepting the normal distribution assumption; such a result is denoted as OK in Table 23.

TABLE 22.

COMPARATIVE ANALYSIS OF BASELINE TAP WATER LEAD DATA

	Los Angeles	Lancaster
Tap Water Sample Lead Concentrations µg/ml	0.040	0.036
	0.019	0.022
	0.024	0.019
	0.021	0.021
	0.028	0.022
Square Root Transformation of Tap Water Lead Data	0.200	0.190
	0.138	0.148
	0.155	0.138
	0.145	0.145
	0.167	0.145
Square Root Transformation Statistics		
Mean	0.161	0.154
Standard Deviation	0.024	0.021
Variance	0.00060	0.00043
Equality of Variance		
F test statistic	1.38	
Variance equality	Yes	
Equality of Means		
t test statistic	0.50	
Mean equality	Yes, (P=.64)	

TABLE 23. Skewness Test of Normal Distribution Under Various Transformations of the Baseline Human Subject Lead Determinations

		Transformation					
		None		Square Root		Natural Log	
Tissue	Group	L. A. P Value	Lanc. P Value	L. A. P Value	Lanc. P Value	L. A. P Value	Lanc. P Value
Blood	Total	<.01	<.01	<.01	.01	OK	OK
	Male	<.01	.01	.03	OK	OK	OK
	Female	<.01	<.01	<.01	.02	OK	OK
Long Hair	Total	<.01	≪.01	<.01	≪.01	OK	OK
	Male	<.01	<.01	.01	<.01	OK	OK
	Female	<.01	≪.01	.04	≪.01	OK	.01
Short Hair	Total	≪.01	<.01	<.01	.02	OK	OK
	Male	<.01	<.01	<.01	OK	OK	OK
	Female	.01	<.01	OK	.03	OK	OK
Urine	Total	<.01	≪.01	<.01	≪.01	OK	<.01
	Male	<.01	<.01	OK	<.01	OK	OK
	Female	<.01	≪.01	<.01	≪.01	OK	<.01
Feces	Total	≪.01	<.01	≪.01	<.01	<.01	OK
	Male	≪.01	<.01	≪.01	.01	<.01	OK
	Female	<.01	<.01	<.01	<.01	<.01	OK

Inspection of Table 23 shows that, for most of the grouped participant lead data, the natural logarithm transformation yields data for which the normal distribution assumption is valid. In those few cases when the natural log transformed data were not normally distributed, it still gave less skewness to the data than either the untransformed or square root transformed data. With respect to the t test's normality assumption, the natural logarithm transformation of the blood, hair, urine, and feces lead data is consistently preferable to either the square root transformation or no transformation.

The validity of the assumption of equality of variance between participants within the two t test compared groups was examined by the standard variance ratio F test. Equality of variance was tested for the comparable groups at the two sites using the untransformed tissue lead data, the square root transformed data, and the natural log transformed data. The F statistic and associated P value are presented for each comparison in Table 24. P values above 0.05 are interpreted as accepting the equality of variance assumption; such P values are simply denoted as OK in Table 24. Examination of Table 24 discloses that the natural log transformation is clearly superior to no transformation or the square root transformation in equalizing the variability within the compared groups. The natural log transformation yielded acceptable variance equality in every case for the blood, urine, and feces lead data. On the long and short hair lead data, the logarithmic transformation was uniformly better than either the square root transformation or no transformation in equalizing the variability of the compared groups.

TABLE 24. Test of Variance Equality Under Various Transformations of the Baseline Human Subject Lead Determinations

		Transformation					
		None		Square Root		Natural Log	
Tissue	Group	F Statistic	P Value	F Statistic	P Value	F Statistic	P Value
Blood	Total	3.32	≪.001	1.94	<.001	1.15	OK
	Male	3.52	<.001	1.98	.005	1.16	OK
	Female	2.53	<.001	1.58	.03	1.02	OK
Long Hair	Total	1.98	<.001	2.07	<.001	1.41	.04
	Male	7.98	≪.001	3.82	<.001	2.35	.004
	Female	1.12	OK	1.55	.04	1.18	OK
Short Hair	Total	31.35	≪.001	6.14	≪.001	1.80	.003
	Male	45.63	≪.001	8.16	≪.001	2.13	.006
	Female	9.38	≪.001	3.57	<.001	1.48	OK
Urine	Total	1.87	<.001	1.04	OK	1.19	OK
	Male	1.92	.009	1.47	OK	1.16	OK
	Female	3.01	<.001	1.22	OK	1.14	OK
Feces	Total	1.44	.02	1.07	OK	1.18	OK
	Male	2.66	<.001	1.31	OK	1.11	OK
	Female	2.71	<.001	1.80	.008	1.29	OK

Since the natural logarithm transformation was so uniformly superior in achieving the t test assumptions, it was applied to each set of compared data prior to the conduct of its t test. To assist in interpreting the results based upon the natural log transformed data, the geometric mean has been reported. The geometric mean is the reverse (i.e., exponential) transformation of the mean of the natural log transformed data back into the original lead concentration data scale.

A summary of the lead concentration data obtained for each sex and age subgroup at the two sites is shown in Tables 25A, 25B, 25C, 25D, and 25E for the five tissues sampled. The data for individual values for lead are provided in Appendix C. The statistics contained in Table 25 are N (the number of participants in the group providing at least one analyzed sample of the tissue), the arithmetic mean of the untransformed data for the group ($\bar{X}$), ± the standard deviation of the arithmetic mean ($s_{\bar{x}} = s / \sqrt{N}$), and the geometric mean.

Table 25 reveals the general characteristics of the lead concentration data from the two baseline sites for each of the five types of samples. The average lead concentrations of the Los Angeles participants were generally higher than those of the corresponding sex and age group of Lancaster participants for the blood, long hair, short hair, and urine samples. However, the average lead concentration in the feces of the Los Angeles participants was about the same or less than the average lead concentration in the Lancaster participants' feces samples.

Table 25A. Baseline Lead Concentration Data Summary

LEAD IN BLOOD, µg/100 ml

	LOS ANGELES			LANCASTER			Significance of Difference
Group	N	Arithmetic Mean (± Std. Dev. of Mean)	Geometric Mean	N	Arithmetic Mean (± Std. Dev. of Mean)	Geometric Mean	P
TOTAL	126	16.4 (± 0.7)	14.6	119	10.5 (± 0.4)	9.6	≪.001
MALES	56	19.3 (± 1.1)	17.2	50	11.8 (± 0.6)	10.8	≪.001
I	20	23.5 (± 2.5)	20.8	21	11.1 (± 0.8)	10.4	≪.001
II	29	16.6 (± 1.1)	15.1	18	11.8 (± 0.7)	10.9	.003
III	7	18.5 (± 2.0)	17.1	11	13.0 (± 2.0)	11.1	.09
FEMALES	70	14.2 (± 0.7)	12.8	69	9.6 (± 0.4)	8.8	≪.001
I	18	16.7 (± 1.8)	14.9	25	10.2 (± 0.7)	9.6	<.001
II	41	12.9 (± 0.6)	11.8	16	9.1 (± 1.2)	8.0	<.001
III	11	14.7 (± 1.5)	13.4	28	9.3 (± 0.5)	8.7	<.001

Table 25B. Baseline Lead Concentration Data Summary

LEAD IN LONG HAIR, µg/g

Group	LOS ANGELES				LANCASTER				Significance of Difference P
	N	Arithmetic Mean (± Std. Dev. of Mean)		Geometric Mean	N	Arithmetic Mean (± Std. Dev. of Mean)		Geometric Mean	
TOTAL	115	44.9	(± 4.3)	27.2	109	19.3	(± 3.1)	12.0	≪.001
MALES	45	43.9	(± 7.8)	24.6	44	21.2	(± 2.8)	16.1	.04
I	18	59.4	(± 9.0)	49.7	20	20.7	(± 3.0)	16.9	≪.001
II	24	35.3	(± 12.7)	15.3	16	20.2	(± 3.5)	16.3	—
III	3	20.5	(± 10.0)	16.4	8	24.6	(± 12.3)	13.9	—
FEMALES	70	45.5	(± 5.0)	29.0	65	18.1	(± 4.9)	9.8	≪.001
I	25	76.7	(± 9.9)	59.6	22	17.3	(± 2.5)	13.7	≪.001
II	35	26.7	(± 3.6)	19.5	17	10.9	(± 1.9)	8.5	.001
III	10	33.2	(± 10.3)	19.3	26	23.4	(± 12.1)	8.0	.06

Table 25C. Baseline Lead Concentration Data Summary

LEAD IN SHORT HAIR, $\mu g/g$

	LOS ANGELES			LANCASTER			Significance of Difference
Group	N	Arithmetic Mean (± Std. Dev. of Mean)	Geometric Mean	N	Arithmetic Mean (± Std. Dev. of Mean)	Geometric Mean	P
TOTAL	94	56.2 (± 7.0)	33.3	88	15.7 (± 1.3)	11.7	≪.001
MALES	50	67.1 (± 12.2)	36.3	45	17.4 (± 1.9)	13.2	≪.001
I	19	107.2 (± 24.9)	74.1	23	16.6 (± 2.5)	12.8	≪.001
II	27	39.5 (± 11.3)	21.5	13	16.9 (± 2.8)	14.2	—
III	4	63.2 (± 28.5)	42.3	9	19.9 (± 6.4)	12.8	.09
FEMALES	44	43.8 (± 6.6)	30.2	43	13.9 (± 1.7)	10.3	≪.001
I	9	70.2 (± 11.8)	63.0	11	12.4 (± 2.6)	10.1	≪.001
II	26	33.4 (± 5.4)	23.7	9	17.8 (± 5.6)	12.3	.07
III	9	47.4 (± 13.6)	29.3	23	13.0 (± 2.1)	9.8	.005

Table 25D. Baseline Lead Concentration Data Summary

LEAD IN URINE, $\mu g/l$

	LOS ANGELES				LANCASTER				Significance of Difference
Group	N	Arithmetic Mean (± Std. Dev. of Mean)		Geometric Mean	N	Arithmetic Mean (± Std. Dev. of Mean)		Geometric Mean	P
TOTAL	136	14.3	(± 0.7)	11.5	121	10.5	(± 1.0)	8.3	≪.001
MALES	59	16.1	(± 1.1)	13.2	51	10.6	(± 0.8)	9.0	<.001
I	23	17.7	(± 1.6)	15.4	21	11.0	(± 1.1)	9.6	.001
II	29	14.9	(± 1.7)	11.6	19	9.0	(± 0.9)	8.0	.01
III	7	15.8	(± 2.5)	13.5	11	12.5	(± 2.9)	9.5	—
FEMALES	77	12.9	(± 0.9)	10.3	70	10.5	(± 1.7)	7.8	.003
I	25	16.4	(± 2.2)	12.6	26	14.7	(± 4.3)	9.7	—
II	41	10.8	(± 0.9)	9.1	16	8.9	(± 1.2)	7.5	—
III	11	12.4	(± 1.8)	10.4	28	7.6	(± 0.8)	6.6	.003

Table 25E. Baseline Lead Concentration Data Summary

LEAD IN FECES, μg/g

Group	LOS ANGELES			LANCASTER			Significanc of Differenc
	N	Arithmetic Mean (± Std. Dev. of Mean)	Geometric Mean	N	Arithmetic Mean (± Std. Dev. of Mean)	Geometric Mean	P
TOTAL	124	0.90 (± 0.09)	0.69	113	1.22 (± 0.08)	0.95	<.001
MALES	52	1.08 (± 0.20)	0.76	46	1.14 (± 0.13)	0.87	—
I	16	1.62 (± 0.59)	1.03	19	1.37 (± 0.23)	1.05	—
II	29	0.84 (± 0.12)	0.66	16	0.97 (± 0.18)	0.81	—
III	7	0.88 (± 0.26)	0.71	11	0.98 (± 0.24)	0.72	—
FEMALES	72	0.76 (± 0.06)	0.64	67	1.27 (± 0.10)	1.01	≪.001
I	21	1.09 (± 0.14)	0.91	24	1.60 (± 0.21)	1.26	.09
II	41	0.67 (± 0.06)	0.58	15	1.34 (± 0.14)	1.16	≪.001
III	10	0.49 (± 0.05)	0.47	28	0.96 (± 0.12)	0.78	.004

The validity of the Table 25 observations was examined utilizing the t test of the logarithmically transformed lead concentration data to determine the significance of the observed differences. The results are presented via the two sided t test statistic and its P value in Table 26.

The mean lead concentrations in the blood, long hair, short hair, and urine of the total group of Los Angeles participants were very significantly higher than the corresponding mean lead concentrations of the total group of Lancaster participants ($P \ll .001$ for each of the four tissues). There was also a significant elevation of the mean blood lead, long hair lead, short hair lead, and urine lead levels of the male and female subgroups of Los Angeles participants over the corresponding Lancaster group. The inferences for the comparable sex-age subgroups across site were less consistent; this finding may be attributable to the smaller sample sizes, the absence of any real difference, or both of these factors. However, in general, the younger age group (1-16) tended to show more significant lead level elevation in Los Angeles than the adult age groups did.

In contrast, the feces lead levels of the Los Angeles participants were significantly lower than those of the Lancaster participants ($P < .001$). This effect was most pronounced for the two adult female groups.

A more detailed statistical description of the site-sex-age groups' lead levels in blood, long hair, short hair, urine, and feces

Table 26. t Test of Significant Mean Lead Concentration Differences between Los Angeles and Lancaster Participants

Tissue	Group	Compared Geometric Means		t Statistic	Significance P Value
		Los Angeles	Lancaster		
Blood µg/100ml	Total	14.6	9.6	8.34	$\ll .001$
	Male	17.2	10.8	6.08	$\ll .001$
	1-16	20.8	10.4	5.42	$\ll .001$
	17-34	15.1	10.9	3.29	.003
	35+	17.1	11.1	1.82	.09
	Female	12.8	8.8	6.14	$\ll .001$
	1-16	14.9	9.6	3.99	$< .001$
	17-34	11.8	8.0	3.80	$< .001$
	35+	13.4	8.7	3.60	$< .001$
Long Hair µg/g	Total	27.2	12.0	6.20	$\ll .001$
	Male	24.6	16.1	2.09	.04
	1-16	49.7	16.9	5.14	$\ll .001$
	17-34	15.3	16.3	-0.19	No
	35+	16.4	13.9	0.24	No
	Female	29.0	9.8	6.35	$\ll .001$
	1-16	59.6	13.7	6.54	$\ll .001$
	17-34	19.5	8.5	3.43	.001
	35+	19.3	8.0	1.99	.06
Short Hair µg/g	Total	33.3	11.7	7.46	$\ll .001$
	Male	36.3	13.2	4.90	$\ll .001$
	1-16	74.1	12.8	7.07	$\ll .001$
	17-34	21.5	14.2	1.22	No
	35+	42.3	12.8	1.86	.09

(Cont'd)

Table 26. (Cont'd)

Tissue	Group	Compared Geometric Means		t Statistic	Significance P Value
		Los Angeles	Lancaster		
Short Hair µg/g (Cont'd)	Female	30.2	10.3	5.73	≪.001
	1-16	63.0	10.1	6.79	≪.001
	17-34	23.7	12.3	1.90	.07
	35+	29.3	9.8	3.03	.005
Urine µg/l	Total	11.5	8.3	5.04	≪.001
	Male	13.2	9.0	4.14	< .001
	1-16	15.4	9.6	3.58	.001
	17-34	11.6	8.0	2.57	.01
	35+	13.5	9.5	1.27	No
	Female	10.3	7.8	3.19	.003
	1-16	12.6	9.7	1.50	No
	17-34	9.1	7.5	1.49	No
	35 +	10.4	6.6	3.14	.003
Feces µg/g	Total	0.69	0.95	-4.13	< .001
	Male	0.76	0.87	-1.02	No
	1-16	1.03	1.05	-0.05	No
	17-34	0.66	0.81	-1.24	No
	35+	0.71	0.72	-0.02	No
	Female	0.64	1.01	-4.89	≪.001
	1-16	0.91	1.26	-1.78	.09
	17-34	0.58	1.16	-5.30	≪.001
	35+	0.47	0.78	-3.04	.004

was developed on computer printouts. These printouts are presented in Appendix E.

Because of concern over possible adverse health effects from the elevated lead levels found in the Los Angeles participants, the sampling of high blood lead concentrations was examined further. The number and percentage of the blood samples with lead concentrations above 40 μg/100 ml are tabulated in Table 27. Only five blood lead concentrations above 40 μg/100 ml were sampled: four from Los Angeles boys aged 8, 8, 10, and 12; one from a 15-year-old Los Angeles girl. The only blood lead level above 50 μg/100 ml was 58.8 μg/100 ml from one of the 8-year-old boys.

The lead concentrations of the blood, hair, urine, and feces samples from the participants at the two sites were also related to various potentially pertinent factors in addition to sex and age. These additional factors were preschool/nursery vs. children in school, length of residence in the city, distance from the expressway, distance from other major highways, type of air conditioning, level of cigarette smoking, ethnic grouping, and occupation. Appendix F presents the geometric lead concentration mean for all levels of each of these factors for each of the five tissues sampled. Examination of Appendix F shows that none of these factors exhibit a consistent effect at both sites. The apparent factor effect generally results from the unequal allocation of the factor among the participants at the two sites, or by correlation of the factor with the sex or age of the participants.

Table 27. Sampling of High Blood Lead Concentrations in Baseline Participants

GROUP			No.of Blood Samples	Samples with Blood Lead above 40μg/100ml	
Site	Sex	Age		Number	Percent,%.
Los Angeles	Male	1-16	23.	4	17
		17-34	56	0	0
		35+	14	0	0
	Female	1-16	29	1	3
		17-34	82	0	0
		35+	21	0	0
Lancaster	Male	1-16	33	0	0
		17-34	34	0	0
		35+	21	0	0
	Female	1-16	43	0	0
		17-34	31	0	0
		35+	54	0	0

Appendix F does suggest possible relationships between some factor/site combinations and the lead concentration for more than one tissue. The Los Angeles preschool and nursery children, who remained in their apartment complex adjacent and downwind from the San Diego Freeway all day, appear to have had slightly higher lead concentrations in their blood, long hair, and short hair than did the older Los Angeles school children (who attended schools at a considerable distance from the expressway). The Los Angeles participants seem to have increased lead levels in their long hair, short hair, and urine with longer lengths of residence in Los Angeles. The Lancaster participants living within two blocks of major highways appear to have higher lead levels in their long and short hair than do the Lancaster participants living farther from major highways. Los Angeles participants living in non-air-conditioned homes seem to have higher lead concentrations in their blood, long hair, and short hair than do the Los Angeles participants whose homes had air conditioning.

The significance of each of these apparent relationships was investigated using a t test. The results are presented in Table 28. There is no significant elevation of the mean lead levels in the blood and hair of the preschool and nursery Los Angeles children over those of the older Los Angeles children. As the participants' length of residence in Los Angeles increased, there was a very significant increase in their mean urine lead level. However, the relationship of mean hair lead to length of residence in Los Angeles remains uncertain. The Los Angeles

Table 28. Significance of Additional Factor Relationships

Site/Factor/Tissue Comparison Groups	No. of Partic.	Geometric Mean	Log. Transformation		Equality of Variance	t Statistic	P Value
			Mean	Std. Dev.			
Los Angeles Schooling							
Blood:							
Preschool and nursery	17	19.6	2.975	0.463	Yes	1.18	.13
Older Children	21	16.4	2.797	0.465			
Long Hair:							
Preschool and nursery	23	61.2	4.114	0.759	Yes	0.99	.17
Older Children	20	49.1	3.893	0.700			
Short Hair:							
Preschool and nursery	15	81.2	4.397	0.863	.04	1.12	.14
Older Children	13	59.6	4.088	0.531			
Length of Residence in Los Angeles							
Long Hair:							
0 or 1 year	28	22.4	3.108	1.054	Yes	1.51	.07
4 yrs or more	39	32.9	3.493	1.010			
Short Hair:							
0 or 1 year	22	24.9	3.216	0.966	Yes	1.39	.08
4 yrs or more	29	37.5	3.624	1.087			
Urine:							
0 or 1 year	29	9.1	2.211	0.488	Yes	3.26	.001
4 yrs or more	47	13.5	2.603	0.523			

(Cont'd)

Table 28. (Cont'd)

Site/Factor/Tissue Comparison Groups	No. of Partic.	Geometric Mean	Log. Transformation		Equality of Variance	t Statistic	P Value
			Mean	Std. Dev.			
Distance from Highway in Lancaster							
Long Hair:							
Less than 2 blocks	23	17.2	2.846	0.772	Yes	2.15	.02
More than 1 mile	51	10.9	2.390	0.873			
Short Hair:							
Less than 2 blocks	20	21.2	3.052	0.656	Yes	3.78	<.001
More than 1 mile	44	10.2	2.320	0.745			
Air Conditioning in Los Angeles							
Blood:							
None	105	15.1	2.711	0.403	Yes	2.09	.02
Window or Central	19	12.2	2.501	0.410			
Long Hair:							
None	97	28.6	3.352	1.013	Yes	1.35	.09
Window or Central	16	19.4	2.964	1.352			
Short Hair:							
None	81	36.1	3.587	0.973	.05	1.86	.03
Window or Central	13	20.1	3.001	1.488			

residents whose homes were air-conditioned had significantly lower average blood and short hair lead levels than the Los Angeles residents living in homes without air conditioning. The Lancaster participants living within two blocks of a major highway had very significantly higher mean short hair lead levels and significantly higher mean long hair lead levels than the Lancaster participants living more than a mile from any major highway. While some of the preceding findings regarding the additional factors are significant, the indicated relationships should not be construed to have been demonstrated. The combination of uncontrolled factors and chance provides a plausible alternative to these significant factors.

c. Autopsy - Los Angeles

Table 29 shows the results of the analysis of autopsy tissues from Los Angeles for lead. As described earlier in this report, these autopsy cases are from a hospital via a pathologist. They are not from accidental death cases. The data are similar to those collected for other lead studies. There are not sufficient samples to describe the lead content with regards to age, sex, length of residency in Los Angeles, smoking history, etc.

d. Sources of Variation in Human Lead Determinations

Two blood, urine, and feces samples were obtained on consecutive days from most of the Los Angeles and Lancaster participants. Table 30 presents the between participant and within

TABLE 29. AUTOPSY TISSUES (Los Angeles)

Lead Values (µg/g - Wet Tissue)

Tissue No.	Kidney	Fat	Spleen	Muscle	Lung	Liver
Male						
1. A 7653	0.00	0.05	1.23	0.06	0.08	1.02
2. A 7593	0.26	0.02	0.28	0.13	0.08	0.53
3. A 7572	0.37	0.13	0.10	0.00	0.00	0.47
4. A 7617	0.59	0.02	1.93	0.03	2.06	1.31
5. A 7657	0.00	0.02	0.11	0.06	0.14	0.64
Female						
6. A 7587	0.05	0.04	0.55	0.02	0.01	0.70
7. A 7658	0.20	0.06	0.12	0.10	0.13	0.54
8. A 7654	0.15	0.00	0.08	0.02	0.12	0.73
9. A 7561	0.45	0.09	0.39	0.39	0.00	0.76
10. A 7621	0.03	0.00	0.15	0.04	0.20	0.63

Table 30. Variance in Participant Groups.

Tissue	Group			Group ln(Pb) Variance		Significant Difference F Test P Value
	Site	Sex	Age	Between Participants	Within Participants	
Blood	Los Angeles	Male	1-16	.2143	.2401	No
			17-34	.1187	.0764	No
			35+	.1154	.0713	No
		Female	1-16	.1716	.1098	No
			17-34	.0973	.0911	No
			35+	.1075	.0888	No
	Lancaster	Male	1-16	.1204	.0347	.02
			17-34	.0951	.0876	No
			35+	.3059	.0451	< .005
		Female	1-16	.0953	.0456	No
			17-34	.1903	.0875	No
			35+	.1163	.0463	.01
Urine	Los Angeles	Male	1-16	.1765	.1416	No
			17-34	.2834	.2115	No
			35+	.2856	.1391	No
		Female	1-16	.4027	.1864	.05
			17-34	.2108	.1295	No
			35+	.2223	.1556	No
	Lancaster	Male	1-16	.1949	.0995	No
			17-34	.1604	.0816	No
			35+	.3627	.1732	No
		Female	1-16	.3405	.1848	No
			17-34	.1853	.1187	No
			35+	.1494	.0889	No

Table 30. Variance in Participant Groups (Cont'd)

Tissue	Group			Group ln(Pb) Variance		Significant Difference F Test P Value
	Site	Sex	Age	Between Participants	Within Participants	
Feces	Los Angeles	Male	1-16	.5889	.2302	No
			17-34	.2880	.1507	No
			35+	.3493	.0971	No
		Female	1-16	.3228	.0726	.01
			17-34	.1856	.0503	<.005
			35+	.0714	.0032	<.005
	Lancaster	Male	1-16	.5352	.0469	<.005
			17-34	.3015	.0518	<.005
			35+	.5433	.0894	.006
		Female	1-16	.4247	.1126	<.005
			17-34	.1749	.1613	No
			35+	.2408	.1492	No

participant variances of the natural log transformed lead determinations within each site-sex-age-group. The P value is tabulated in the last column of Table 30 for those groups having a significantly smaller within group variance than the between group variance. In most groups, there was no significant difference. The implication in these cases is that the two samples obtained on consecutive days from one person display about as much variability in their lead determinations as two samples taken from two different people in the same group. The within group (i.e., diurnal/sampling/analytical) variability is very large.

An additional blood sampling experiment was performed to investigate the source of the within group variability. Sixteen blood samples were obtained simultaneously from an adult male and processed and analyzed according to the same procedures used with the baseline blood samples. Two aliquots of each sample were processed and analyzed; their lead determinations are presented in Table 31. An analysis of variance of the logarithmically transformed blood lead determinations is shown in Table 32. There are no significant differences between the aliquots or between the samples.

The variance components estimated from the sampling experiment have been compared against the participant and sampling variances for the appropriate group (males aged 17 to 34) of Lancaster and Los Angeles participants. The comparison is shown in Table 33. The repeatability variance accounts for about 13% of the between

Table 31. Blood Lead Determinations from Sampling Experiment

	Blood Lead, µg/100 ml	
Sample	Aliquot A	Aliquot B
1	5.86	7.19
2	7.74	7.35
3	6.28	7.67
4	6.77	9.02
5	6.09	6.88
6	6.76	6.92
7	6.99	7.02
8	9.42	7.39
9	7.12	7.25
10	9.32	7.79
11	7.10	8.60
12	6.36	6.90
13	6.18	7.35
14	8.17	7.35
15	7.99	6.18
16	7.99	9.89

Table 32. Analysis of Variance of Natural Log Blood Lead Determinations

$$\text{Model: } Y_{ij} = \mu + A_i + B_j + \epsilon_{ij}$$

Source	Sum of Squares	df	Mean Square	F-Ratio
Between Samples	0.2968	15	0.0198	1.35
Between Aliquots	0.0145	1	0.0145	0.99
Residual	0.2202	15	0.0147	
Total	0.5315	31		

Table 33. Sources of Blood Lead Variability. $Y=\ln(Pb)$

Source	Degrees of Freedom	Estimated Variance	Percent of Between Participant Total
Between participants (Los Angeles and Lancaster males aged 17-34)	45	0.1098	
Between samples from a participant (taken on consecutive days)	43	0.0806	73.4%
Between samples (taken simultaneously)	15	0.0198	18.0%
Residual (Processing/ analytical method repeatability)	16	0.0147	13.4%

participant variance. The simultaneous sampling variance accounts for another 5%. The variability associated with sampling on consecutive days contributes another 55% to the between participant variance. Apparently there was much daily variability in the blood lead levels of the participants in this study.

The individual blood lead analysis results are presented in Appendix C. In regard to sampling variation, a scan of the data disclosed that all 15 sampled blood lead concentrations above 30 μg/100 ml occurred in the first sample provided by Los Angeles participants. Most of the elevated blood lead values occurred in children, some of whom were not sampled for blood on the second day. Thus, of the Los Angeles participants who provided two blood samples, there were 10 blood lead concentrations above 30 μg/100 ml; in each of these ten cases, the first sample concentration analysis was above 30 μg/100 ml, and the second sample value was below 30 μg/100 ml. This anomaly was investigated further to determine whether there was a consistent lead concentration bias between the first and second samples of the Los Angeles and/or Lancaster participants.

A review of the blood shipment and lead analysis procedures did not detect any erroneous blood lead values. The sequence in which the lead analyses of the blood samples were performed was the only facet of the lead analysis procedure that might be relevant to the anomaly. All of the first samples were analyzed before any of the second samples. However, to prevent a site bias, the Los Angeles and

Lancaster first sample lead analyses were properly interspersed; so were the second sample lead analyses.

The cumulative sample distributions of the lead concentration determinations for the 99 Los Angeles participants and the 97 Lancaster participants who provided two blood samples are shown below. For both Los Angeles and Lancaster, more of the high blood

	Los Angeles		Lancaster	
	First Sample	Second Sample	First Sample	Second Sample
# Samples 30μg/100ml	10	0	0	0
# Samples 25μg/100ml	16	5	0	1
# Samples 20μg/100ml	28	14	3	5
# Samples 15μg/100ml	47	40	19	9
# Samples 10μg/100ml	70	79	48	36
# Samples 5μg/100ml	98	97	90	91
Total Number of Samples	99	99	97	97

lead determinations occurred on the first sample than on the second sample. The two-sample Kolmogorov-Smirnov Test was utilized to test for significant differences between the first sample and second sample distributions. Neigher for Los Angeles (D = .182; P = .08) nor for Lancaster (D = .144; P = .27) did the first sample and the second sample distributions differ significantly at the 0.05 level.

Lancaster first sample lead analyses were properly interspersed; so were the second sample lead analyses.

The cumulative sample distributions of the lead concentration determinations for the 99 Los Angeles participants and the 97 Lancaster participants who provided two blood samples are shown below. For both Los Angeles and Lancaster, more of the high blood lead determinations occurred on the first sample than on the second sample. The two-sample Kolmogorov-Smirnov Test was utilized to test for significant differences between the first sample and second sample distributions. Neigher for Los Angeles (D = .182; P = .08) nor for Lancaster (D = .144; P = .27) did the first sample and the second sample distributions differ significantly at the 0.05 level.

		Los Angeles		Lancaster	
		First Sample	Second Sample	First Sample	Second Sample
# Samples	30µg/100ml	10	0	0	0
# Samples	25µg/100ml	16	5	0	1
# Samples	20µg/100ml	28	14	3	5
# Samples	15µg/100ml	47	40	19	9
# Samples	10µg/100ml	70	79	48	36
# Samples	5µg/100ml	98	97	90	91
Total Number of Samples		99	99	97	97

The mean and standard deviation of these paired sample lead determinations are presented below, for both the value and their natural logarithm transformations. Because the blood lead

	Los Angeles		Lancaster	
	First Sample	Second Sample	First Sample	Second Sample
Number of Samples	99	99	97	97
Original Values, µg/100ml				
Mean	16.45	14.22	10.71	9.96
Standard Deviation	9.80	5.29	4.68	4.45
Ln Transformation, ln (µg/100 ml)				
Mean	2.652	2.582	2.262	2.212
Standard Deviation	0.539	0.400	0.506	0.414

determinations have a skewed distribution, t tests utilizing the natural logarithm transformed values should be employed to test for bias between the first and second sample lead determinations. Since the sample determinations are paired, the paired comparison t test is the most powerful for detecting shifts in the distribution. The two-sided paired comparison t test of the logarithmically transformed blood lead determinations shows no significant difference in means between the first sample and the second sample, neither for Los Angeles (t = 1.17; P = .25) nor for Lancaster (t = 1.00; P = .32). While the preponderance of the high Los Angeles blood lead determinations occurred on the first sample, the statistical analysis of the paired samples discloses no significant differences between the first sample determinations and the second sample determinations, neither in their overall distribution nor in their location. There is no detectable bias between the first sample and the second sample determinations.

e. ^{210}Pb Analysis

^{210}Pb has been used as a tracer to determine the sources of lead present in people.(27) Terhaar and Aronow (27) selected children with elevated blood leads that were known to have consumed leaded paint and compared them with children with low blood leads without exposure to leaded paint. They examined urine and feces samples from these children for Pb and ^{210}Pb. Their study was designed to determine whether or not lead from dust was contributing to the body burdens of lead in the children that were eating leaded paint. ^{210}Pb is very low in paint chips (0.005-0.07 p Ci/g), much higher in airborne particulate (60-150 p Ci/g) and also high in dusts (3-30 p Ci/g).

From these data, it would appear that the following probably would occur in different situations.

	Blood		Feces	
Major Sources of Lead	Pb	^{210}Pb	Pb	^{210}Pb
Paint	high	low	high	low
Dust	high	high	high	high
Air	high	high	low	low
Low lead exposure (dietary only)	low	low	low	low

Reports in the literature have not demonstrated all of these relationships, especially with respect to blood. In this project, samples of blood and feces were collected from children at the UCLA site, along with particulate air and soil samples, for ^{210}Pb analysis. The objective was to obtain additional information relative to the sources of lead at this site.

Airborne particulate samples yielded the following results:

Los Angeles - UCLA site 1. 137 p Ci/g
UCLA site 2. 157 p Ci/g

These values are similar to those reported for urban airborne particulate (60-150 p Ci/g).

The ratio of ^{210}Pb to ^{208}Pb (stable) in the air particulate matter collected at Los Angeles (UCLA site) is:

$$\frac{\text{pCi } ^{210}\text{Pb}}{\text{mg } ^{208}\text{Pb}} = 3.012 \text{ average}$$

Applying this ratio to a 10-ml blood sample containing approximately 40μg of stable lead per 100 ml of blood, there would be 0.012 p Ci ^{210}Pb present. The detection limit of the method for ^{210}Pb was 0.045 p Ci (average) for total blood sample, and the detection limit for 10g feces (dry wt.) was 0.05 p Ci/g.

Only one of the 30 blood samples analyzed for ^{210}Pb was positive. The blood sample had 18.7 μg of stable lead per 100 ml of whole blood, and 1.6 p Ci of ^{210}Pb/10 ml of blood was found. The other blood samples were less than the detection limit. Of the thirty feces samples examined three had detectable levels.

These values were:

pCi/g	stable Pb Mg/g (wet)
0.18	2.22
0.026	--
0.040	1.21

A value of 0.044 pCi/g has been reported by TerHaar and Aronow as a normal fecal ^{210}Pb value.

The data for soil samples are as follows:

Sample Identification	^{210}Pb-pCi/g (dry wt.)	Stable Pb µg/g (dry wt.)
100 ft. west of freeway	1. 0.66 2. 0.86	1. 58 2. 96
20 ft. east of freeway	1. 1.09 2. 0.96	1. 3490 2. 3775
100 ft. east of freeway	1. 1.22 2. 0.99	1. 824 2. 522
300 ft. east of freeway	1. 0.57 2. 0.74	1. 165 2. 302

The results from these analysis are not as useful as was expected because the detection limits obtained were not sufficiently low. The air particulate samples and soil data are similar to those reported elsewhere. The fecal values are low, as was expected, but the data for blood are not useful because the sensitivity was not good enough. A high average for blood would have been 0.012 p Ci per 10 ml, but the detection limit of the method was only 0.045 pCi per 10 ml.

More information is needed on this type of measurement to prove its usefulness in defining the sources of lead. It has been shown by TerHaar and Aronow that the measurements will differentiate in children with high blood and high fecal leads as to consumption of lead primarily from paint or soils. Its usefulness has not been demonstrated for airborne lead.

B. Mining

1. Environment

Air, water (from streams and ponds) and soil samples were collected in an around the mining and ore processing facilities located in Sudbury, Ontario. Most of these samples did not produce measurable responses with AA. Table 34 shows the air data. The precious metals area is located within the ore processing part of the plant, and this area includes the final step performed by this plant on platinum and palladium concentrates. Measureable levels were found in surface soil samples located in two areas around the plant.

	Soil	
	Pt	Pd
Vermillion Mine	0.8 ppb	4.5 * ppb
Copper Cliff	0.8 ppb	2.0 * ppb

* limit of detection 0.7 ppb

Water samples were negative for platinum and palladium, and the detection limits are as follows: platinum 0.05 ppb, palladium 0.015 ppb.

Table 34. Platinum and Palladium Concentrations in Air Samples at the Sudbury Mine

Location within the Mine	Metal Concentration, µg/m^3	
	Platinum	Palladium
Engineering Building	a	a
South Mine	a	a
Precious Metals Area	0.377	0.291
Furnace Room	a	a

a. Below detection limit of 0.003 µg/m^3

2. Study Participants

As mentioned earlier in this report 49 male employees in mining and ore processing at Sudbury were sampled twice for blood, urine, and feces. A sample of short and long hair was also collected. These samples were examined for content of platinum and palladium, and no detectable levels were found. The detection limits for these types of samples were given in Table 5.

3. Autopsy Cases

A total of nine male autopsy cases were collected in Sudbury from individuals that had been previously employed by the mining and ore processing plants in this area. Table 35 shows information collected on these cases. Samples of liver, kidney, spleen, lung, muscle and fat were collected from each autopsy. In all but the following samples, there were no detectable levels of platinum and palladium.

Sample ID	Pt
A 120-75 - fat	4.5 ppb
A 100-75 - lung	3.7 ppb
A 114-75 - muscle	25.0 ppb

C. Refineries

1. Environment

In one of the refineries (samples collected and analyzed by the company), it was reported that 42 air samples were collected in 15 different locations within the plant over a 9-month period. The values

TABLE 35. AUTOPSY CASES - SUDBURY

Sample ID	Age	Sex	Smoking History	Cause of Death
A 52-75	50	M	Unknown	Skull fracture
A 59-75	60	M	Yes	Coronary infraction
A 70-75	55	M	Unknown	Coronary thrombosis
A 73-75	73	M	Unknown	Coronary thombosis
A 99-75	61	M	Unknown	Myocardial infraction
A 100-75	52	M	Unknown	Ischemic heart
A 106-75	47	M	Yes	Coronary thrombosis
A 114-75	22	M	Yes	Automobile accident
A 120-75	51	M	Yes	Pulmonary edema/ischemia

for platinum and palladium were very low and in all cases were within the prescribed OSHA standards as set forth in the Federal Register, Vol. 36, No. 157, dated August 31, 1971.

In the other refinery, the samples were collected by the company but analyzed by this laboratory.

The working environment of the refinery was characterized through 24-hour ambient air samples collected for five consecutive work days in the refinery and salts sections of the plant. The platinum and palladium concentration determinations obtained in the air sampling are presented in Table 36. Note the relatively high palladium air determination obtained on Monday in the refinery work section. This air sample, whose palladium concentration was at least 0.356 $\mu g/m^3$, probably represents a valid palladium determination. However, because of the possibility of contamination, the statistics for the refinery area palladium data set were calculated both including and excluding the Monday sample. Table 36 shows weekly average platinum concentrations of 0.159 $\mu g/m^3$ and 0.180 $\mu g/m^3$ and palladium concentrations of 0.085 $\mu g/m^3$ and 0.028 $\mu g/m^3$, respectively, in the refinery and salts sections. Without the Monday sample, 0.017 was the weekly average palladium concentration in the refinery section. In general, the platinum concentration appears to have been higher than the palladium concentration in the air inside this refinery. However, all the measured ambient air levels of platinum and palladium were well below the OSHA standards.

Table 36. Platinum and Palladium Concentrations in Air Samples at the New Jersey Precious Metals Refinery

	Metal Concentration, µg/m^3			
	Platinum		Palladium	
	Refinery Section	Salts Section	Refinery Section	Salts Section
Air Sampler Determinations				
Monday	0.113	0.133	0.356[a]	0.057
Tuesday	0.240	0.211	0.013	0.015
Wednesday	0.259	0.182	0.008	0.003
Thursday	0.161	0.168	0.043	0.048
Friday	0.021	0.205	b	0.016
Weekly Statistics				
No. of samples	5	5	5/4*	5
Mean	0.159	0.180	0.085/ 0.017*	0.028
Standard Deviation	0.097	0.031	0.153/ 0.018*	0.023

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a. Estimate value - the result exceeded the linear calibration range

b. Below the 0.003 µg/m^3 detection limit

* Excluding the Monday sample

2. Study Participants

One of the refineries examined 17 of their employees (substantially all of whom by the nature of their work were involved in operations associated with the chemical processing of platinum and palladium) for platinum and palladium in urine and blood samples. No platinum or palladium was found. The detection limits given (by the refinery) were 60 ppb for platinum and 20 ppb for palladium.

Samples of blood and urine were collected from 61 refinery workers by the other refinery and analyzed in this laboratory. The levels of platinum and palladium in blood were below the detection limits (1.4 ppb platinum and 0.4 ppb palladium).

Six of the 58 urine samples obtained and analyzed had platinum concentrations above the detection limit of 0.10 μg/l. These six determinations which ranged from 0.23 μg/l to 2.58 μg/l are presented in Table 37. It is noteworthy that each urine sample with a detectable platinum concentration also had a palladium level above 1.0 μg/l. The workers with detectable platinum levels were not confined to any particular work section within the refinery.

Thirty-four of the 58 workers submitting urine samples had urine palladium concentrations above the 0.21 μg/l detection limit. The sample determinations are presented by refinery work section in Table 38. The mean and standard deviation of the palladium determinations for each work section and for the total refinery are also shown in Table 38. The mean palladium urine concentration was 1.07 μg/l; the maximum

Table 37. Platinum Concentrations in Urine Samples from the Six New Jersey Refinery Workers with Detectable Platinum Levels

Urine Platinum Concentration µg/l	Worker's Work Section	Corresponding Urine Palladium Concentration, µg/l
0.23	Maintenance	1.59
0.49	Refinery	2.93
0.66	Refinery	1.05
1.22	Salts	2.42
1.24	Salts	6.27
2.58	Storeroom	7.41

Notes:

The urine samples of 58 refinery workers were analyzed for platinum.

The minimum detectable urine platinum concentration was 0.10 µg/l.

TABLE 38. NEW JERSEY REFINERY WORKER URINE PALLADIUM CONCENTRATIONS CLASSIFICATION BY REFINERY WORK SECTION

	Urine Palladium Concentration, µg/l					
	Refinery Work Section					
	Refinery	Mills	Recovery	Maintenance	Storeroom	Refinery Total
Sample Determinations:	a	a	0.43	0.77	a	
	2.12	5.91	a	2.83	7.41	
	0.81	a	0.34	0.28	a	
	0.35	a	a	a		
	1.08	a	0.28	a		
	a	1.28	0.36	a		
	1.05	0.95	6.67	1.59		
	a	a	0.27	0.87		
	2.93	2.42	a	0.60		
	a	6.27	0.41	2.09		
	a	0.63	a	1.66		
	0.31		0.25	0.46		
			a			
			a			
			a			
			1.38			
			0.77			
			a			
			0.62			
			a			
Statistics:						
No. of Samples	12	11	20	12	3	58
Mean	0.80	1.68	0.68	1.03	2.61	1.07
Std. Dev.	0.88	2.28	1.44	1.03	4.16	1.68

a Below minimum detectable urine palladium concentration of 0.21 µg/l determination was 7.41 μg/l. The urine samples were collected overnight Monday and returned on Tuesday. Despite the high air palladium concentration in the refinery section on Monday, Table 38 does not indicate any obvious relationship between a worker's work area and his urine palladium concentration.

The original urine palladium data presented in Table 38 and their natural logarithm transformations have been examined with respect to the normality of their distribution. The logarithmically transformed data, having a mean of -0.67 and a standard deviation of 1.09 over all 58 observations, is much less skewed. The assumption that this logarithmically transformed data has a normal distribution appears to be warranted.

A one-way analysis of variance by refinery work section was conducted on the natural log transformed urine palladium concentration data. Table 39 presents the mean and standard deviation of the natural log transformed data in each refinery work section. The logarithmic transformation does tend to equalize the urine palladium variability within each work section. Table 39 also contains the analysis of variance by work section. There was no significant difference in the mean urine palladium concentration among the workers in the five refinery work sections ($F = 0.991 < F_{.05}(4,53) = 2.55$). In fact, there is just as much urine palladium variability among the workers within a single work section as between workers in different work sections.

Table 39. The One-Way Analysis of Variance of Logarithmically Transformed Urine Palladium Concentrations by Refinery Work Section.

Urine Palladium Statistics Under Natural Log Transformation.	Refinery Work Section				
	Refinery	Salts	Recovery	Maintenance	Storeroom
Sample Size	12	11	20	12	3
Mean	-0.70	-0.33	-1.02	-0.43	-0.37
Standard Deviation	0.98	1.36	0.86	1.01	2.06

ANALYSIS OF VARIANCE

	Sum of Squares	DF	Mean Square	F Ratio
Between Sections	4.704	4	1.176	0.991*
Within Sections	62.875	53	1.186	
Total	67.580	57		

*Not significant. $F_{.05}(4,53) = 2.55$

Correlation analysis was used to explore any relationship of the urine palladium determinations to the available social and occupational variables. Table 40 presents the results of the correlation analysis of the logarithmically-transformed urine palladium determinations with the age, race, cigarette smoking, length of employment, work section, and work shift or the refinery worker participants. The correlation analysis shown in Table 40 was conducted both for all 58 workers with analyzed urine samples and for the 34 workers with detectable urine palladium levels. There are no significant correlations of urine palladium with any of these six factors for either worker data set. The variability in the workers' urine palladium concentrations cannot be explained in terms of the available social and occupational factors.

Table 40. Correlation of Log-Transformed Urine Lead Concentrations of Refinery Workers with Various Occupational and Social Factors.

Worker Set	Factor	Number of Pairs	Correlation Coefficient, r	P Value	Significant Correlation?
All Workers with Analyzed Urine Samples	Age	58	-0.101	.45	No
	Race	58	-0.179	.18	No
	Cigarette Smoking	58	0.092	>.50	No
	Length of Employment	58	-0.006	>.50	No
	Work Section	58	0.028	>.50	No
	Work Shift	58	0.023	>.50	No
All Workers with Detectable Palladium Levels in their Urine Samples	Age	34	-0.062	>.50	No
	Race	34	0.001	>.50	No
	Cigarette Smoking	34	-0.221	.20	No
	Length of Employment	34	0.217	.22	No
	Work Section	34	0.031	>.50	No
	Work Shift	34	0.079	>.50	No

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APPENDIX A

INDIVIDUAL INFORMATION ON PARTICIPANTS FROM LOS ANGELES AND LANCASTER

LOS ANGELES BY ID NUMBER

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0101[illegible]222335        22      1260[illegible]   7005
0106[illegible]22223310601033 22     204[illegible]2000
0107[illegible]22223310813073 22     2045[illegible]   000
0108[illegible]222335        22      1041[illegible]2000
0109[illegible]222336        22      1041[illegible]   000
0110[illegible]222335        22      1041[illegible]   000
0111[illegible]222335        22      1040[illegible]2000
0112[illegible]233336        22      1030[illegible]20005
0114[illegible]233333        11117   1242[illegible]   0005
0115[illegible]22223310604013 11412  2263[illegible]27005
0116[illegible]2222320900073 22      1052[illegible]   0005
0118[illegible]3333310603041 22      6095[illegible]20255
0119[illegible]121335        22      13405[illegible]   000
0120[illegible]2323110607083 11115   51335[illegible]   0053
0121[illegible]1213310601041 22      33425[illegible]21000
0124[illegible]1312120603041 22      2058[illegible]21005
0125[illegible]13131106050627 22115  2058[illegible]   0005
0126[illegible]131315        22      1051[illegible]   0005
0127[illegible]131315        22      1051[illegible]   0005
0128[illegible]131315        22      1051[illegible]27005
0129[illegible]131315        22      1050[illegible]20005

0130[illegible]131316        22      1300[illegible]   0005
0131[illegible]32223310818061 12 18382074[illegible]   003
0132[illegible]3222331060604 1 121[illegible]207[illegible]22000
0133[illegible]322335        22      10712[illegible]2000
0134[illegible]322335        22      10710[illegible]2000
0135[illegible]32133106121 11 12519382064[illegible]   700
0140  321335                 22      1361[illegible]2005
0141[illegible]3213310810041 11425   2065[illegible]2025
0142[illegible]3213310903113 22      1072[illegible]2025
0143[illegible]222331        22      11520[illegible]   000
0144[illegible]222339        1231624 21642[illegible]22000
0145[illegible]222337        22      11604[illegible]   000
0146[illegible]222333        22      503[illegible]2000
0147[illegible]22233105   003 22     405[illegible]2005
0148[illegible]2323210601021 11414   25620[illegible]   000
0150[illegible]323315        22      10714[illegible]222000
0151[illegible]232324        22      25627[illegible]221000
0152[illegible]232327        22      1360[illegible]   000
0153[illegible]333322100007б 121116161151[illegible]   000
0154[illegible]232334        22      2264[illegible]22020
0155[illegible]232335        22      1251[illegible]   000
0160[illegible]3323121102073 22      1051[illegible]   000
0162[illegible]231335        22  —   1051[illegible]   100  ?
0164[illegible]2313311000073 22      1051[illegible]   000
0165[illegible]2313310606013 11318   2094[illegible]2000
0167[illegible]3323110612033 22  —   405[illegible]222700
0168[illegible]233315        22      1210[illegible]212000
0169[illegible]233317        22      1010[illegible]   000
0170[illegible]233319        22      2252[illegible]2000
0171[illegible]2333111000031 22      2292[illegible]   000
0172[illegible]233335        22      1151[illegible]   000
0173[illegible]233334        11313   2451[illegible]2000
0174[illegible]23     311403041 12319372195[illegible]   100
0175[illegible]233336        11320   2295[illegible]   003
0450[illegible]322336        11 53   2016[illegible]   0005
0451[illegible]222315        22      1160[illegible]21005
0452[illegible]222317        22      1160[illegible]   7005
0453[illegible]433335        22      1171[illegible]   0005
0454[illegible]433336        22      1171[illegible]20005
0455[illegible]433335        22      1170[illegible]   0005
0456[illegible]433335        22      1170[illegible]   0005
```

APPENDIX B

DETERMINATION OF SAMPLE SIZE TO ANALYZE VACUTAINER CONTAMINATION STUDY

A 95% Confidence interval around a true mean value, μ, is given by:

$$\bar{X} - (1.96)\left(\frac{\sigma}{\sqrt{n}}\right) \leq \mu \leq \bar{X} + (1.96)\left(\frac{\sigma}{\sqrt{n}}\right)$$

where

$\bar{X}$ = sample mean

σ = standard deviation

n = sample size

(1.96) = table value for a large enough n.

The length of the interval, L, is the difference between the two limits, or

$$L = 2(1.96)\left(\frac{\sigma}{\sqrt{n}}\right)$$

This implies that

$$\frac{1}{n} = \frac{L^2}{4\,(1.96)^2\ \sigma^2}$$

or

$$n = 15.366\left(\frac{\sigma^2}{L^2}\right)$$

If we set a desired length of the interval (L), then knowing σ^2 we can determine the sample size necessary to achieve that length. From previous work with the procedure used for blood lead analysis, we know the standard deviation (σ) of the method if approximately 1.3 μg/100 ml. From this, a sample size of 40 will provide an interval of 0.8 μg/100 ml.

APPENDIX C

INDIVIDUAL LEAD VALUES FOR PARTICIPANTS FROM LOS ANGELES AND LANCASTER

Blood-Lead Raw Data
μg/100 ml whole blood

Sample I.D.	Sample No. 1	Sample No. 2
201	14.67	---
207	10.33	19.91
208	13.12	9.25
209	25.50	29.02
210	11.54	10.34
211	9.03	13.65
212	23.75	3.63
213	20,35	7.30
214	18.92	21.76
215	34.98	12.35
216	18.24	8.18
217	9,92	7.37
218	22.35	11.06
220	27.92	---
221	14.93	20.41
222	12.35	18.12
223	17,22	---
224	19.98	---
225	13.50	---
226	9.03	12.85
227	9.76	---
230	24.96	---
231	39.92	---
232	11.87	5.47
233	8.49	7.87
234	13.51	28.40
235	21,08	9.02
237	12.53	19.14
240	---	---
241	7.44	5.65
242	16.26	19.62
243	20.31	8.21
244	---	---
245	21,22	---
246	16.95	---
247	21,28	---
248	19.57	12.51
249	20.94	20.69
250	16.12	15.95
251	15.43	16.07
252	17.84	20.22

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Sample I.D.	Blood-Lead Raw Data μg/100 ml whole blood	
	Sample No. 1	Sample No. 2
253	30.12	20.88
254	---	---
255	42.39	---
256	15.97	12.54
257	18.46	---
258	---	---
259	11.33	3.63
260	10.45	8.25
265	22.06	25.28
266	13.50	16.71
267	14.61	---
268	19.34	12.71
269	27.16	12.35
270	38.45	13.25
271	11.37	8.60
272	---	---
273	12.45	20.57
274	23.70	---
275	33.37	11.77
276	9.25	---
277	49.41	---
278	58.83	20.18
279	16.73	16.03
280	11.83	13.09
281	15.36	13.07
282	49.36	19.51
283	20.78	13.53
285	18.34	14.99
286	---	---
287	12.24	9.07
288	23.92	---
289	31.13	---
290	6.67	14.49
291	27.41	11.00
297	36.58	15.04
298	5.89	10.45
302	26.56	15.40
303	---	---
304	32.57	14.99
305	7.07	18.02
306	23.15	10.23

LOS ANGELES, CALIFORNIA

Blood-Lead Raw Data
µg/100 ml whole blood

Sample I.D.	Sample No. 1	Sample No. 2
307	16.47	---
309	---	---
310	9.88	10.27
311	9.25	8.53
312	9.89	10.87
313	33.78	15.07
400	15.96	27.08
401	11.43	---
402	40.79	17.73
403	9.88	14.58
404	14.33	11.40
405	8.67	15.74
406	4.75	16.88
407	10.21	---
408	15.84	18.77
410	29.57	13.08
411	16.66	19.03
412	5.77	8.06
413	11.12	13.09
414	11.49	12.75
415	11.03	8.98
416	5.11	10.32
417	9.31	15.80
418	8.09	---
419	21.55	11.31
420	12.47	<1.50
421	15.93	19.38
422	22.12	13.66
423	5.13	11.16
424	12.00	11.26
425	6.40	9.14
426	16.94	7.75
427	9.58	19.97
428	23.92	26.04
430	7.76	14.39
431	9.21	16.61
432	8.99	10.01
433	15.39	16.58
434	4.95	17.35
435	8.40	11.76
436	6.79	12.11

LOS ANGELES, CALIFORNIA

Blood-Lead Raw Data
μg/100 ml whole blood

Sample I.D.	Sample No. 1		Sample No. 2
437	7.25		22.28
438	8.91		10.37
439	13.12		---
440	18.70		---
441	---		---
442	10.87		9.35
443	<1.50	omit	<1.50
444	25.41		---
445	9.21		14.23
446	12.90		10.34
447	12.39		15.18
448	13.13		20.90
449	15.31		19.25

LOS ANGELES, CALIFORNIA

Feces-Lead Raw Data
µg/g wet weight

Sample I.D.	Sample No. 1	Sample No. 2
201	--	0.54
207	--	0.28
208	0.01	0.58
209	1.70	3.31
210	0.83	1.78
211	0.65	0.42
212	0.71	0.81
213	1.00	0.80
214	0.62	2.04
215	0.48	0.29
216	0.08	1.18
217	--	0.97
218	0.24	0.41
219	1.20	3.83
220	0.69	2.62
221	0.62	3.57
222	2.11	--
223	0.30	--
224	0.41	1.17
225	--	0.86
226	0.23	0.14
227	0.29	0.01
230	--	--
231	--	--
232	--	0.65
233	0.30	0.29
234	--	0.18
235	0.19	0.30
239	0.29	1.48
240	--	10.19
241	0.52	0.51
242	0.23	0.38
243	0.17	0.23
244	2.07	--
245	0.46	0.61
246	--	0.76
247	0.53	1.61
248	1.54	0.65
249	--	0.73
250	0.37	0.83
251	--	0.17
252	0.20	0.61
	1.99	

LOS ANGELES, CALIFORNIA

Sample I.D.	Feces-Lead Raw Data µg/g wet weight Sample No. 1	 Sample No. 2
253	4.71	1.48 5.40
254	1.98	2.37
255	0.53	2.22
256	0.31	0.41
257	--	--
258	--	--
259	0.25	0.19
260	0.91	1.08
265	--	1.21
266	--	0.84
267	0.40	1.09
268	0.22	0.11
269	--	0.56
270	0.00	0.05
271	1.62	0.84
272	--	--
273	0.62	1.15
274	0.77	--
275	0.65	0.85
276	--	--
277	--	--
278	--	1.22
279	0.42	--
280	0.81	--
281	1.64	1.00
282	--	2.40
283	1.69	--
285	--	0.26
286	1.54	--
287	0.10	0.37
288	--	1.51
289	0.30	--
290	0.61	0.22
291	--	0.29
297	0.60	1.84
298	0.47	0.73
302	0.42	0.48
303	--	--
304	3.22	1.56

Feces-Lead Raw Data
µg/g wet weight

Sample I.D.	Sample No. 1	Sample No. 2
305	0.90	1.40
306	0.57	0.56
307	0.41	0.87
309	--	--
310	0.14	0.78
311	0.98	1.02
312	0.48	0.16
313	0.30	0.97
400	0.48	0.41
401	--	0.77
402	--	1.10
403	0.53	0.01
404	0.60	0.18
405	--	1.20
406	2.49	1.32
407	0.69	0.70
408	0.47	0.55
410	0.48	0.58
411	0.27	0.71
412	0.29	0.17
413	0.33	0.02
414	--	0.21
415	0.64	--
416	0.64	0.52
417	--	0.01
418	0.30	0.79
419	0.54	0.28
420	0.15	0.11
		0.87
421	0.36	0.10
422	0.79	0.37
423	0.58	0.56
424	0.64	1.09
425	0.66	0.48
426	0.37	0.65
427	0.49	0.47
428	0.28	0.59
430	0.42	--
431	--	0.27
432	0.38	0.77

LOS ANGELES, CALIFORNIA

	Feces-Lead Raw Data µg/g wet weight	
Sample I.D.	Sample No. 1	Sample No. 2
433	--	0.85
434	0.93	0.55
435	0.30	0.30
436	0.53	0.31
437	0.70	0.84
438	1.21	0.76
439	--	--
440	0.83	1.41
441	--	--
442	0.46	--
443	0.96	--
444	--	--
445	--	--
446	0.24	--
447	--	0.08
448	--	0.80
449	0.91	--

LOS ANGELES, CALIFORNIA

Hair-Lead Raw Data
µg/g

Sample I.D.	Short Hair	Long Hair
201	26.67	11.51
207	12.05	27.52
208	4.32	4.54
209	--	124.49
210	14.47	--
211	24.66	14.31
212	5.74	7.45
		3.62
213	6.49	2.83
214	--	14.30
215	--	73.63
216	23.34	--
217	--	--
218	37.29	--
219	--	72.34
220	101.37	38.05
221	28.15	--
222	--	27.63
223	136.47	--
224	47.75	--
225	155.52	--
226	79.49	--
227	54.86	--
230	52.10	54.25
231	82.32	71.33
232	35.39	42.30
233	50.21	--
234	23.03	37.39
235	6.20	5.92
239	45.63	21.71
240	--	148.14
		157.19
241	13.26	31.98
242	308.59	280.34
		271.89
		378.74
243	12.58	17.77
244	--	180.87
		169.10
		199.01

LOS ANGELES, CALIFORNIA

Sample I.D.	Hair-Lead Raw Data μg/g Short Hair	Long Hair
245	--	120.36
		137.32
246	38.30	51.34
247	26.17	22.99
248	44.01	40.84
249	89.89	130.03
	145.37	103.03
250	109.14	88.91
251	69.49	--
252	--	33.90
253	9.03	18.61
254	--	47.65
255	62.77	59.36
256	14.27	--
257	25.91	27.65
258	--	73.44
259	7.61	21.17
260	<0.70	3.24
265	33.16	25.35
266	63.84	61.03
267	37.00	48.63
268	--	9.33
269	3.08	6.36
270	8.97	13.19
271	22.72	3.63
272	41.99	14.17
273	71.24	--
274	310.10	--
275	80.23	--
276	--	100.54
277	275.41	--
278	408.16	--
279	68.90	85.24
280	51.78	77.62
281	21.98	20.55
282	53.68	50.86
283	50.89	39.32
285	42.09	--
286	--	146.71

LOS ANGELES, CALIFORNIA

Hair-Lead Raw Data
µg/g

Sample I.D.	Short Hair	Long Hair
287	--	43.78
288	151.37	148.67
289	36.55	55.33
290	--	9.44
291	--	40.23
297	31.46	19.47
298	--	57.50
302	32.06	22.75
303	58.99	46.85
304	18.80	13.01
305	43.15	21.72
		22.55
306	--	14.30
307	--	112.15
309	56.87	68.48
310	8.33	7.90
311	28.10	6.64
312	--	65.61
313	49.61	17.20
400	--	28.66
401	--	45.48
402	--	177.27
		225.60
403	--	80.94
404	--	31.00
405	--	30.63
406	--	22.92
407	100.76	72.31
408	--	22.88
410	104.00	29.80
411	133.44	8.35
412	--	9.37
413	8.79	3.74
414	--	23.25
415	--	12.36
416	--	31.20
417	3.82	86.67
	86.67	99.12

LOS ANGELES, CALIFORNIA

Sample I.D.	Hair-Lead Raw Data µg/g Short Hair	Long Hair
418	26.49	17.18
419	--	28.03
420	--	59.63
421	--	14.31
422	14.97	--
423	31.08	19.38
424	30.98	5.30
425	[illegible]0.70	1.27
426	28.89	13.51
427	14.12	5.08
428	85.47	--
430	79.81	4.51
431	--	9.48
432	27.02	29.08
433	88.00	46.49
434	14.34	13.95
435	10.23	6.37
436	10.96	7.69
437	29.74	7.48
438	21.64	41.40
439	--	97.84
440	--	72.10
441	114.07	154.40
442	48.89	22.97
443	--	80.14
444	51.00	35.46
445	8.35	1.76
446	37.17	12.23
447	--	18.62
448	--	--
449	107.33	94.94
		121.15

Urine-Lead Raw Data

µg/l

Sample I.D.	Sample No. 1	Sample No. 2
201	14.3	8.8
207	2.7	3.9
208	7.2	10.7
	8.3	
209	13.5	5.8
210	13.1	3.9
211	5.4	17.4
212	5.7	11.4
213	10.9	6.9
214	23.0	37.6
215	18.7	8.5
216	37.5	5.0
217	5.4	--
218	4.4	5.6
220	10.3	6.6
221	2.7	7.2
222	2.7	7.6
223	11.4	9.0
224	22.1	18.0
225	6.6	14.8
226	2.1	5.4
227	5.0	--
230	26.3	15.1
231	19.7	--
232	33.7	17.8
233	5.2	19.4
234	33.2	12.2
		11.3
		8.4
235	25.9	5.2
239	33.7	22.9
240	11.6	34.9
241	4.7	15.5
242	3.3	5.5
243	12.5	14.0
244	18.8	13.5
245	11.0	9.2
246	19.7	35.0
247	25.1	12.7
248	14.1	9.0
249	24.4	11.6
250	<0.6	--

LOS ANGELES, CALIFORNIA

Sample I.D.	Urine-Lead Raw Data µg/l Sample No. 1	Urine-Lead Raw Data µg/l Sample No. 2
251	15.6	11.7
252	31.7	15.3
253	77.4	19.3
254	3.2	10.7
255	9.6	9.9
256	13.0	7.8
257	32.4	16.6
258	--	25.2
259	1.7	11.2
260	7.7	6.4
265	35.2	10.1
		11.3
266	9.8	6.8
267	11.6	6.1
268	4.5	3.6
269	9.3	2.4
270	7.3	21.8
271	26.2	25.7
272	17.0	14.1
273	2.1	20.9
274	38.7	--
275	--	18.6
		13.2
276	9.6	29.7
277	34.3	18.3
278	18.2	22.6
279	39.7	--
280	6.7	--
281	2.3	11.3
282	4.6	25.4
283	25.7	19.2
285	--	23.7
286	3.2	36.3
287	4.7	12.8
288	6.6	15.1
289	10.8	26.7
290	6.3	6.6
291	13.2	23.1
297	6.2	5.4
298	2.2	9.2
302	3.6	13.9

LOS ANGELES, CALIFORNIA

Urine-Lead Raw Data
µg/l

Sample I.D.	Sample No. 1	Sample No. 2	
303	<0.6	6.0	
304	30.1	18.5	
305	25.8	10.2	
306	2.6	8.5	
307	7.7	14.1	
309	--	13.1	
310	36.2	6.3	
311	7.4	1.6	
312	10.7	6.5	
	11.6		
313	20.9	8.0	
400	6.6	[illegible].9	8.7
401	21.4	14.0	
402	25.3	22.3	
403	27.5	4.0	
404	3.7	10.2	
405	2.7	4.7	
406	5.9	13.3	
407	20.0	12.2	
408	15.3	18.0	
410	7.9	11.2	
411	15.2	3.6	
412	11.6	10.6	
413	6.8	2.4	
414	11.6	6.0	
415	13.7	9.2	
		10.4	
416	0.7	3.6	
417	12.5	4.4	
418	13.0	17.6	
419	7.2	10.7	
420	3.3	11.9	
421	12.6	10.0	
422	22.0	7.3	
423	14.3	4.9	
424	24.5	5.7	
425	18.2	13.6	
426	12.3	14.8	
427	16.8	16.9	
428	25.5	19.5	
430	4.3	19.5	
431	26.7	13.4	

	Urine-Lead Raw Data µg/l	
Sample I.D.	Sample No. 1	Sample No. 2
432	<0.6	12.1
433	10.8	18.3
434	12.3	8.0
435	--	9.6
436	7.6	16.0
437	--	4.7
438	17.6	14.1
439	44.7	15.1
440	9.8	17.8
441	76.0	23.8
442	3.4	24.5
443	5.2	21.8
444	13.5	16.1
445	9.8	17.8
446	5.2	4.1
447	--	4.9
448	18.6	13.1
449	17.9	27.3

Lancaster, California

LANCASTER, CALIFORNIA

	Blood-Lead Raw Data µg/100 ml whole blood	
Sample I.D.	**Sample No. 1**	**Sample No. 2**
001	13.65	8.24
002	10.73	---
006	7.78	6.63
007	---	24.43
008	14.75	13.69
010	10.17	9.97
011	12.31	11.57
012	16.34	8.27
013	15.39	5.97
014	4.62	15.56
016	13.89	5.78
023	5.98	9.19
028	8.85	9.09
029	6.40	9.31
030	7.38	10.46
031	16.34	6.81
034	12.46	6.92
036	13.46	12.80
038	8.01	9.73
043	4.35	5.61
044	14.04	---
045	14.61	12.45
046	6.43	4.93
052	17.56	---
053	9.03	13.68
054	8.16	13.14
055	11.12	5.68
056	12.74	8.12
057	10.74	7.01
058	9.16	7.62
063	8.23	5.59
064	10.32	8.59
066	<1.50	3.01
067	5.47	8.66
068	9.45	8.05
069	8.98	7.20
070	12.31	10.04
071	15.48	6.54
072	8.87	11.29
073	21.28	---
074	8.14	7.20

Blood-Lead Raw Data
µg/100 ml whole blood

Sample I.D.	Sample No. 1	Sample No. 2
075	13.40	16.44
079	12.45	3.84
080	7.88	8.17
081	7.32	9.30
083	9.16	9.95
084	9.16	8.15
085	6.75	9.09
087	<1.50	5.49
088	16.96	12.62
089	15.61	6.60
090	16.97	9.66
091	9.63	7.35
094	15.90	16.82
096	---	---
097	14.84	5.34
098	5.00	14.89
099	8.26	8.87
100	10.49	14.53
106	9.18	14.53
107	11.12	7.10
108	6.97	5.15
109	8.27	14.65
110	21.29	20.18
111	6.09	4.85
112	14.11	8.43
114	21.76	25.34
115	24.17	24.86
116	15.03	5.73
118	14.23	8.91
119	12.29	---
120	8.71	6.73
121	3.28	6.92
124	5.44	11.10
125	17.49	24.38
126	5.01	4.76
127	15.63	12.37
128	9.12	7.01
129	9.03	---
130	8.51	---
131	4.65	7.92
132	12.52	13.25
133	10.01	10.89

LANCASTER, CALIFORNIA

Sample I.D.	Blood-Lead Raw Data µg/100 ml whole blood Sample No. 1	Blood-Lead Raw Data µg/100 ml whole blood Sample No. 2
134	11.95	12.77
139	18.47	7.15
140	13.48	---
141	10.85	7.21
142	9.93	11.35
143	13.39	<1.50
144	5.91	12.45
145	8.31	---
146	13.70	6.47
147	12.07	12.19
149	7.51	12.25
150	5.11	6.01
151	4.22	8.05
152	7.96	---
153	19.94	10.77
154	5.82	4.45
155	17.96	12.66
160	12.19	12.69
163	12.19	7.29
164	9.42	9.92
165	5.55	8.89
167	9.46	---
168	8.88	---
169	11.71	---
170	5.53	---
171	---	10.78
172	11.59	13.33
173	6.69	9.85
174	6.69	6.35
175	18.47	20.70
450	18.86	18.38
451	7.56	---
452	6.40	---
453	5.91	8.13
454	8.51	---
455	7.94	---
456	9.87	---

LANCASTER, CALIFORNIA

Feces-Lead Raw Data
µg/g wet weight

Sample I.D.	Sample No. 1	Sample No. 2
001	0.37	0.35
002	0.29	0.49
006	0.22	0.11
007	0.59	1.60
008	0.70	0.54
010	1.29	1.08
011	1.10	--
012	0.86	0.44
013	0.96	0.73
014	0.33	0.60
016	2.14	1.94
023	5.07	0.69
028	0.95	1.17
029	0.65	0.59
030	5.41	2.38
031	--	2.13
034	0.95	2.18
035	2.06	--
036	0.96	--
038	--	0.77
043	0.40	0.02
044	1.22	1.91
045	1.30	1.67
046	1.53	0.74
050	--	--
052	4.02	--
053	0.44	0.61
		0.32
054	0.81	0.44
055	1.16	0.67
056	2.54	0.25
057	0.92	1.65
058	3.63	1.49
063	0.39	0.29
064	0.46	0.62
066	0.64	0.35
		0.26
067	1.51	2.61
068	1.27	0.52
069	--	0.48

LANCASTER, CALIFORNIA

Sample I.D.	Feces-Lead Raw Data µg/g wet weight Sample No. 1	Sample No. 2
070	<1.50	0.36
071	0.86	1.09
	0.44	
072	1.58	0.97
073	1.78	3.50
074	0.24	0.43
075	0.31	0.32
076	0.58	--
079	0.72	--
080	1.08	0.51
081	0.85	1.28
083	0.64	2.56
084	--	--
085	0.88	0.31
		0.13
087	1.40	3.78
088	--	--
089	--	--
090	2.65	4.29
091	2.02	1.38
094	1.18	1.19
096	3.14	1.66
097	0.29	0.43
098	2.06	1.68
099	--	0.33
100	1.11	1.38
101	--	--
106	1.57	0.33
107	0.42	0.36
108	2.48	3.09
109	2.38	2.85
110	2.04	0.46
		0.53
111	0.94	0.56
112	1.44	2.63
114	1.18	0.75
115	--	--
116	0.67	1.40
118	0.86	0.47
119	1.01	0.66

LANCASTER, CALIFORNIA

Feces-Lead Raw Data
μg/g wet weight

Sample I.D.	Sample No. 1	Sample No. 2
120	0.99	1.30
121	1.49	1.46
124	1.27	--
125	3.47	1.46
126	0.37	--
127	3.04	3.45
128	2.67	0.58
129	1.31	0.94
130	1.12	1.07
131	2.28	1.42
132	2.82	1.30
133	2.10	1.58
134	3.94	1.79
139	1.42	0.54
140	--	--
141	0.42	--
142	0.60	0.42
143	0.73	0.47
144	1.38	0.06
145	0.09	0.50
146	0.04	0.16
147	0.67	0.93
149	1.17	0.63
150	2.29	2.00
151	0.84	1.09
152	1.24	1.32
153	1.26	0.67
154	0.86	1.24
155	0.33	1.11
160	0.84	1.16
163	3.71	--
164	--	--
165	1.23	0.91
167	1.16	0.33
		0.22
168	1.14	0.92
169	0.45	0.15
170	1.10	--
171	--	0.44
172	0.56	0.57
173	0.78	0.84

Feces-Lead Raw Data
µg/g wet weight

Sample I.D.	Sample No. 1	Sample No. 2
174	0.40	1.03
175	0.20	--
450	0.20	0.00
451	1.04	--
452	1.10	--
453	--	--
454	0.45	--
455	--	0.68
456	--	--

LANCASTER, CALIFORNIA

Sample I.D.	Hair-Lead Raw Data µg/g Short Hair	Long Hair
001	--	14.91
002	2.71	13.05
006	2.95	3.90
007	13.64	9.83
008	13.59	2.77
010	10.37	--
011	<0.70	20.05
012	6.69	9.07
013	15.11	11.43
014	--	3.39
016	8.29	1.75
017	20.78	--
023	22.94	23.60
028	9.42	4.48
029	9.25	13.35
030	--	12.16
031	10.06	7.61
	8.37	
034	43.34	16.12
035	14.98	--
036	--	7.76
038	3.57	7.12
	3.48	
043	<0.70	--
044	7.98	14.78
	11.69	
045	5.80	13.35
	8.14	
046	4.93	2.61
	5.03	
050	--	4.01
052	--	44.40
053	41.39	42.78
054	--	14.38
055	43.51	98.76
		121.48
056	--	9.08
057	16.27	12.87

LANCASTER, CALIFORNIA

	Hair-Lead Raw Data µg/g	
Sample I.D.	**Short Hair**	**Long Hair**
063	--	--
064	4.00	10.27
066	14.33	15.79
067	14.10	29.08
068	27.01	6.21
069	7.20	<0.70
070	14.34	9.14
071	7.88	13.60
072	3.78	4.22
	4.51	
073	13.08	22.82
074	13.36	9.86
075	2.21	3.10
	1.76	
079	--	53.45
080	5.78	7.31
081	7.51	9.75
083	--	4.71
084	2.83	5.33
	4.88	13.84
	4.10	
085	16.17	12.26
087	12.92	7.33
088	1.12	15.99
089	--	13.22
090	24.93	24.19
091	20.39	5.01
094	24.58	34.06
096	26.75	22.53
097	--	28.02
098	--	28.65
099	--	17.06
100	--	3.57
101	5.83	16.61
106	4.20	6.42
107	9.48	9.88
108	5.09	--
109	7.11	17.84
110	--	15.47

LANCASTER, CALIFORNIA

Hair-Lead Raw Data
µg/g

Sample I.D.	Short Hair	Long Hair
111	5.93	5.99
112	27.51	39.61
114	--	--
115	--	2.70
		<0.70
116	12.28	12.51
118	4.23	2.42
119	19.51	27.12
120	24.14	24.48
121	--	24.68
124	47.85	16.63
125	56.41	--
126	16.32	8.37
127	19.88	10.17
128	--	27.84
129	--	34.35
130	45.80	--
131	2.54	<0.70
		4.81
132	--	0.94
		<0.70
133	--	6.63
134	--	--
139	46.79	108.52
140	19.87	18.29
141	7.40	4.27
142	22.67	14.07
143	40.57	42.51
144	9.78	9.49
145	942.00	131.35
146	764.00	3826.80
	819.00	
147	--	312.07
149	7.92	8.59
150	13.45	6.46
151	--	15.45
152	22.23	28.25
153	10.31	25.58
154	10.76	3.91
		3.33

LANCASTER, CALIFORNIA

Hair-Lead Raw Data
µg/g

Sample I.D.	Short Hair	Long Hair
155	20.89	80.78
160	11.95	9.01
163	29.06	42.65
164	27.68	14.36
165	16.46	5.08
		2.67
		3.80
167	6.90	3.71
168	--	33.49
169	16.11	--
170	8.69	8.35
	12.67	
171	11.37	24.03
172	22.59	15.22
173	--	7.78
174	--	40.70
175	20.20	11.73
450	--	4660.70
451	--	19.14
452	14.01	16.39
453	31.19	39.40
454	--	13.50
455	5.96	7.94
456	9.31	10.24

LANCASTER, CALIFORNIA

Sample I.D.	Urine-Lead Raw Data µg/l Sample No. 1	 Sample No. 2
001	17.0	9.1
002	7.4	12.7
006	---	8.5
007	46.8	28.9
008	1.3	5.6
010	20.0	8.8
011	2.5	27.3
012	---	2.1
013	20.4	6.3
014	5.3	<0.6
016	12.8	8.5
023	1.4	3.5
028	---	9.8
029	5.9	5.0
030	8.5	3.6
031	11.5	7.0
034	9.2	4.8
036	4.1	4.4
038	10.0	<0.6
043	6.0	5.2
044	8.3	10.1
045	14.0	--
046	20.0	4.4
052	18.5	14.0
053	13.5	1.6
054	3.6	<0.6
055	19.5	12.4
056	4.7	1.4
057	9.7	8.9
058	8.8	11.0
063	6.6	0.8
064	5.7	<0.6
066	2.3	<0.6
C67	4.1	2.5
068	6.0	4.3
069	1.4	1.2
070	5.6	5.3
		6.5
071	11.3	--
072	12.5	4.8
073	21.3	11.9

LANCASTER, CALIFORNIA

Sample I.D.	Urine-Lead Raw Data µg/l Sample No. 1	Sample No. 2
074	9.5	7.3
078	0.8	2.9
079	14.4	11.5
080	6.8	2.0
081	5.8	19.7
083	20.7	9.9
084	9.0	12.1
086	7.0	<0.6
087	9.7	1.0
088	19.4	11.7
089	32.4	209.2
090	9.7	5.3
091	5.9	7.0
094	22.1	4.7
096	26.5	16.2
097	---	9.9
098	6.6	--
099	10.4	<0.6
100	12.4	8.7
106	2.3	37.2
107	4.8	7.8
108	19.9	<0.6
109	5.7	6.3
110	11.0	6.6
111	13.1	3.2
112	13.8	10.2
114	6.3	5.9
115	6.8	6.3
116	16.7	19.1
118	3.0	3.0
119	10.4	3.3
120	7.0	4.7
121	<0.6	6.3
124	4.6	2.9
125	3.6	2.3
126	9.6	<0.6
127	10.3	3.3
128	3.5	11.0
129	7.5	16.4
130	3.7	11.2
131	32.5	0.8
132	<0.6	2.3
133	30.5	9.1
134	6.5	<0.6

LANCASTER, CALIFORNIA

Sample I.D.	Urine-Lead Raw Data ug/l Sample No. 1	Urine-Lead Raw Data ug/l Sample No. 2
139	12.9	14.2
140	21.0	3.9
141	11.7	9.2
142	13.1	2.4
143	7.8	0.7
144	<0.6	2.1
145	27.7	7.5
146	9.2	8.7
147	--	12.1
149	17.3	10.2
150	6.8	1.7
151	31.5	14.5
152	33.5	19.0
153	2.7	4.6
154	4.7	5.3
155	11.6	14.7
160	7.7	4.2
163	12.9	14.5
164	11.0	9.8
165	<0.6	2.9
167	7.4	2.5
168	5.9	<0.6
169	26.0	9.3
170	7.4	5.5
171	--	8.2
172	11.6	9.3
173	4.9	3.2
174	2.0	1.7
175	20.8	<0.6
451	12.2	6.8
452	13.6	8.6
453	12.9	--
454	6.4	--
455	2.5	--
456	7.0	--
450	12.3	--
060	--	3.7

APPENDIX D

THE LABELING CODE

The Label Code (15 Characters)

Columns	Variable	Format	Valid Codes
1-4	Human subjects identification number	4N	Four digit ID number taken from subject's questionnaire
	Location code	4AN	Location of air or dust samples
	Soil Location Code	4AN	S is the first character; columns 2-4 are sequential numbers
	Water Location Code	4AN	W is the first character; columns 2-4 are sequential numbers.
	Sewage Location Code	4AN	R is the first character; Columns 2-4 are sequential numbers.
5	Sample medium	1AN	A - Air sample B - Blood Sample D - Dust Sample F - Feces Sample H - Hair sample (out from scalp) I - Inner Hair Sample (close to scalp) R - Raw sewage sample S - Soil sample T - Throat swab sample U - Urine sample W - Water sample Z - Sputum sample 1 - Abdominal fat sample (umbilical area) 2 - Psoas muscle sample 3 - Liver (right lobe) 4 - Pancreas (tail) 5 - Kidney cortex
6	Sample analysis	1AN	(blank) - General (Collection) A - antibodies B - bacteria H - mercury M - trace metals P - parasites V - viruses
7-8	Site	2AN	Site identifying code CH - Chicago LA - Los Angeles LC - Lancaster, California NJ - New Jersey

Columns	Variable	Format	Valid Codes
9	Sampling period	1N	1,2,3,4,5,6
10	Sampling subperiod (day) (Site samples) or sample number (human subject samples)	1N	1,2,3,4,5,6,7,8,9
11	Sampling sub-subperiod (Air, and dust samples)	1N	(blank), 1,2,3,4,5,6,7,8,9
12-15	Project number	4N	3881, 4005, 4007, etc.

METAL ANALYSIS CODING FORM

Label Code	[illegible]	[illegible]	Analysis 1	Analysis 2	Analysis 3	Analysis 4	Analysis 5	Analysis 6	[illegible]
[illegible]	[illegible]	[illegible]	Value	Value	Value	Value	Value	Value	[illegible]

APPENDIX E

ANALYSES VARIABLES IN LEAD

ANALYSIS VARIABLE: LEAD

SPECIFIED TISSUES: BLOOD HAIR-LONG HAIR-SHORT URINE FECES

TRANSFORMATIONS: LOGARITHMIC LOGARITHMIC LOGARITHMIC LOGARITHMIC LOGARITHMIC

CHARACTERISTIC SEQUENCE: SITE SEX AGE

LN LEAD IN BLOOD , LN(UG/100ML)

CHARACTERISTIC(S) 1	2	3	*	LEVEL VALUE(S) 1	2	3	*	NO. PART.	MEAN	STANDARD DEVIATION	COEF. VAR.	VARIANCE	NO. DUPL.	S.E. VAR.
SITE				LOSANGELES				126	2.6886	.4076	.1517	.1662	44	.1881
SITE				LANCASTER				119	2.2618	.3783	.1673	.1431	47	.1157
SITE	SEX			LOSANGELESMALE				56	2.8958	.4110	.1419	.1689	37	.1779
SITE	SEX			LOSANGELESFEMALE				70	2.6479	.3529	.1333	.1245	60	[illegible]
SITE	SEX			LANCASTER MALE				50	2.3756	.3812	.1605	.1453	20	.1196
SITE	SEX			LANCASTER FEMALE				69	2.1776	.3564	.1636	.1270	54	.1178
SITE	SEX	AGE		LOSANGELESMALE		1-16		20	3.0256	.4921	.1626	.2421	1	[illegible]
SITE	SEX	AGE		LOSANGELESMALE		17-34		29	2.7171	.3445	.1268	.1187	27	[illegible]
SITE	SEX	AGE		LOSANGELESMALE		35+		7	2.8365	.3395	.1197	.1154	7	[illegible]
SITE	SEX	AGE		LOSANGELESFEMALE		1-16		10	2.7004	[illegible]	[illegible]	.1736	11	[illegible]
SITE	SEX	AGE		LOSANGELESFEMALE		17-34		41	2.4694	.3119	.1263	.0973	41	[illegible]
SITE	SEX	AGE		LOSANGELESFEMALE		35+		11	2.5950	.3280	.1264	.1076	10	[illegible]
SITE	SEX	AGE		LANCASTER MALE		1-16		21	2.3462	.3470	[illegible]	.1204	18	[illegible]
SITE	SEX	AGE		LANCASTER MALE		17-34		10	2.3908	.3084	.1290	.0951	16	.1762
SITE	SEX	AGE		LANCASTER MALE		35+		11	2.4108	[illegible]	[illegible]	.0954	10	.0903
SITE	SEX	AGE		LANCASTER FEMALE		1-16		26	2.2613	.3087	.1365	.0953	10	.0412
SITE	SEX	AGE		LANCASTER FEMALE		17-34		16	2.0767	.4361	.2100	.1902	16	.1781
SITE	SEX	AGE		LANCASTER FEMALE		35+		28	2.1622	.3410	.1577	.1163	26	.0427

```
LN LEAD      IN  HAIR-LONG ,   LN(UG/GM     )

        CHARACTERISTIC(S)                       LEVEL VALUE(S)                      NO.     MEAN    STANDARD   COEF.   VARIANCE  NO.    N.P.
  1         2         3        *         1            2            3       *      PART.            DEVIATION  VAR.               DUPL.   VAR.
SITE                                 LOSANGELES
SITE                                 LANCASTER                                   115    3.3037    1.0694    .3237    1.1437   0    0.0000
                                                                                 109    2.4817     .9020    .3635     .8137   0    0.0000
SITE      SEX                        LOSANGELESMALE
SITE      SEX                        LOSANGELESFEMALE                             45    3.2030    1.1291    .3525    1.2749   0    0.0000
SITE      SEX                        LANCASTER MALE                               70    3.3689    1.0329    .3065    1.0669   0    0.0000
SITE      SEX                        LANCASTER FEMALE                             44    2.7792     .7371    .2652     .5434   0    0.0000
                                                                                  65    2.2803     .9518    .4174     .9060   0    0.0000
SITE      SEX       AGE              LOSANGELESMALE        1-16                   18    3.9051     .6217    .1592     .3866   0    0.0000
SITE      SEX       AGE              LOSANGELESMALE        17-34                  29    2.7276    1.2052    .4419    1.4525   0    0.0000
SITE      SEX       AGE              LOSANGELESMALE        35+                     3    2.7942     .8107    .2901     .6572   0    0.0000
SITE      SEX       AGE              LOSANGELESFEMALE      1-16                   25    4.0878     .8066    .1973     .6506   0    0.0000
SITE      SEX       AGE              LOSANGELESFEMALE      17-34                  35    2.9709     .8468    .2850     .7171   0    0.0000
SITE      SEX       AGE              LOSANGELESFEMALE      35+                    10    2.9611    1.2211    .4124    1.4910   0    0.0000
SITE      SEX       AGE              LANCASTER MALE        1-16                   20    2.8278     .6660    .2355     .4436   0    0.0000
SITE      SEX       AGE              LANCASTER MALE        17-34                  16    2.7919     .6753    .2419     .4560   0    0.0000
SITE      SEX       AGE              LANCASTER MALE        35+                     8    2.6335    1.0609    .4028    1.1255   0    0.0000
SITE      SEX       AGE              LANCASTER FEMALE      1-16                   22    2.6196     .7202    .2749     .5187   0    0.0000
SITE      SEX       AGE              LANCASTER FEMALE      17-34                  17    2.1415     .7534    .3518     .5677   0    0.0000
SITE      SEX       AGE              LANCASTER FEMALE      35+                    26    2.0838    1.1686    .5608    1.3657   0    0.0000
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LN LEAD IN HAIR-SHORT, LN(UG/GM)

CHARACTERISTIC(S) 1	2	3	4	LEVEL VALUE(S) 1	2	3	4	NO. PART.	MEAN	STANDARD DEVIATION	COEF. VAR.	VARIANCE	NO. DUPL.	D.F. VAR.
SITE				LOSANGELES				97	3.5060	1.0825	.3088	1.1717	0	0.0000
SITE				LANCASTER				88	2.4546	.7453	.3036	.5556	0	0.0000
SITE	SEX			LOSANGELES	MALE			50	3.5919	1.1623	.3236	1.3510	0	0.0000
SITE	SEX			LOSANGELES	FEMALE			44	3.4041	.9587	.2816	.9191	0	0.0000
SITE	SEX			LANCASTER	MALE			45	2.5783	.7966	.3090	.6346	0	0.0000
SITE	SEX			LANCASTER	FEMALE			43	2.3343	.7839	.3358	.6146	0	0.0000
SITE	SEX	AGE		LOSANGELES	MALE	1-16		19	4.6688	.8993	.1926	.8087	0	0.0000
SITE	SEX	AGE		LOSANGELES	MALE	17-34		27	3.0658	1.1269	.3676	1.2700	0	0.0000
SITE	SEX	AGE		LOSANGELES	MALE	35+		4	3.7939	1.0806	.2848	1.1677	0	0.0000
SITE	SEX	AGE		LOSANGELES	FEMALE	1-16		4	4.1931	.9441	.2252	.8913	0	0.0000
SITE	SEX	AGE		LOSANGELES	FEMALE	17-34		26	3.1663	.8916	.2816	.7950	0	0.0000
SITE	SEX	AGE		LOSANGELES	FEMALE	35+		9	3.2765	1.1731	.3580	1.3761	0	0.0000
SITE	SEX	AGE		LANCASTER	MALE	1-16		23	2.5480	.7800	.3061	.6084	0	0.0000
SITE	SEX	AGE		LANCASTER	MALE	17-34		13	2.6317	.6667	.2533	.4444	0	0.0000
SITE	SEX	AGE		LANCASTER	MALE	35+		9	2.5994	1.0669	.4104	1.1383	0	0.0000
SITE	SEX	AGE		LANCASTER	FEMALE	1-16		11	2.3084	.6778	.2936	.4594	0	0.0000
SITE	SEX	AGE		LANCASTER	FEMALE	17-34		9	2.3188	.5968	.2574	.3562	0	0.0000
SITE	SEX	AGE		LANCASTER	FEMALE	35+		23	2.2741	.8103	.3563	.6566	0	0.0000

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                                LN LEAD     IN URINE    ,   LN(UG/L     )

        CHARACTERISTIC(S)               LEVEL VALUE(S)                NO.     MEAN   STANDARD  COEF.   VARIANCE  NO.   V.P.
   1          2          3     *      1            2        3    *   PART.          DEVIATION  VAR.             DUPL.  VAR.
  SITE                               LOSANGELES                       136    2.4983    .6387   .0183   .4044182        .0030
  SITE                               LANCASTER                        121    2.1168    .4344   .0311   .1846186        .0064

  SITE       SEX                     LOSANGELESMALE                    59    2.5769    .5012   .1948   .0512 94        .0080
  SITE       SEX                     LOSANGELESFEMALE                  77    2.3159    .5370   .0301   .0083 88        .0001
  SITE       SEX                     LANCASTER MALE                    51    2.1933    .4644   .0180   .2161 91        .0250
  SITE       SEX                     LANCASTER FEMALE                  70    2.0546    .5003   .0434   .2591 65        .0630

  SITE       SEX        AGE          LOSANGELESMALE    1-16            23    2.7319    .4801   .1688   .1988 61        .2232
  SITE       SEX        AGE          LOSANGELESMALE    17-34           29    2.4476    .5123   .2175   .2630 87        .4041
  SITE       SEX        AGE          LOSANGELESMALE    35+              7    2.6041    .5308   .2056   .2856  6        .2708
  SITE       SEX        AGE          LOSANGELESFEMALE  1-16            25    2.5307    .6346   .2507   .4067 40        .1780
  SITE       SEX        AGE          LOSANGELESFEMALE  17-34           41    2.2186    .5594   .2077   .2100 38        .2544
  SITE       SEX        AGE          LOSANGELESFEMALE  35+             11    2.3459    .4718   .2018   .2223 18        .3112
  SITE       SEX        AGE          LANCASTER MALE    1-16            21    2.2660    .4419   .1948   .1944 15        .1231
  SITE       SEX        AGE          LANCASTER MALE    17-34           19    2.0746    .4008   .1940   .1609 16        .1630
  SITE       SEX        AGE          LANCASTER MALE    35+             11    2.2506    .6022   .2679   .3627 10        .0469
  SITE       SEX        AGE          LANCASTER FEMALE  1-16            26    2.2760    .5236   .2566   .2466 40        .0847
  SITE       SEX        AGE          LANCASTER FEMALE  17-34           16    2.0121    .5305   .2149   .1053 15        .2276
  SITE       SEX        AGE          LANCASTER FEMALE  35+             28    1.8861    .3848   .2044   .1444 26        .1774
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                              LN LEAD     IN FECES     ,     LN(UG/GM     )

        CHARACTERISTIC(S)                      LEVEL VALUE(S)                   NO.     MEAN     STANDARD  COEF.  VARIANCE  NO.   S.E.
  1          2          3        *       1          2          3        *     PART.             DEVIATION VAR.             SUPL.  VAL.
 SITE                                 LOSANGELES                                1?0   [illegible]  [illegible]    [illegible]      [illegible]
 SITE                                 LANCASTER                                 113   [illegible]  [illegible]    [illegible]      [illegible]

 SITE       SEX                       LOSANGELESMALE                             58   [illegible]  [illegible]    [illegible]      [illegible]
 SITE       SEX                       LOSANGELESFEMALE                           78   [illegible]  [illegible]    [illegible]      [illegible]
 SITE       SEX                       LANCASTER MALE                             66   [illegible]  [illegible]    [illegible]      [illegible]
 SITE       SEX                       LANCASTER FEMALE                           67   [illegible]  [illegible]    [illegible]      [illegible]

 SITE       SEX        AGE            LOSANGELESMALE       1-16                  16   [illegible]  [illegible]    [illegible]      [illegible]
 SITE       SEX        AGE            LOSANGELESMALE       17-39                 29   [illegible]  [illegible]    [illegible]      [illegible]
 SITE       SEX        AGE            LOSANGELESMALE       39+                    9   [illegible]  [illegible]    [illegible]      [illegible]
 SITE       SEX        AGE            LOSANGELESFEMALE     1-16                  21   [illegible]  [illegible]    [illegible]      [illegible]
 SITE       SEX        AGE            LOSANGELESFEMALE     17-39                 61   [illegible]  [illegible]    [illegible]      [illegible]
 SITE       SEX        AGE            LOSANGELESFEMALE     39+                   18   [illegible]  [illegible]    [illegible]      [illegible]
 SITE       SEX        AGE            LANCASTER MALE       1-16                  19   [illegible]  [illegible]    [illegible]      [illegible]
 SITE       SEX        AGE            LANCASTER MALE       17-39                 16   [illegible]  [illegible]    [illegible]      [illegible]
 SITE       SEX        AGE            LANCASTER MALE       39+                   11   [illegible]  [illegible]    [illegible]      [illegible]
 SITE       SEX        AGE            LANCASTER FEMALE     1-16                  29   [illegible]  [illegible]    [illegible]      [illegible]
 SITE       SEX        AGE            LANCASTER FEMALE     17-39                 18   [illegible]  [illegible]    [illegible]      [illegible]
 SITE       SEX        AGE            LANCASTER FEMALE     39+                   28   [illegible]  [illegible]    [illegible]      [illegible]
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APPENDIX F

EFFECT OF ADDITIONAL FACTORS ON LEAD CONCENTRATION

Effect of Additional Factors on Lead Concentration

Factor	Levels	Tissue	(No. of Participants), Geometric Lead Mean					
			Total Baseline		Los Angeles		Lancaster	
Schooling	Preschool	Blood µg/100 ml	(5)	10.1			(5)	10.1
	Preschool + Nursery		(17)	19.6	(17)	19.5		
	Others under 17		(62)	11.8	(21)	16.4	(41)	10.0
	Preschool	Long Hair µg/g	(3)	21.9			(3)	21.9
	Preschool + Nursery		(23)	61.2	(23)	61.2		
	Others under 17		(59)	22.1	(20)	49.0	(39)	14.7
	Preschool	Short Hair µg/g	(4)	16.0			(4)	16.0
	Preschool + Nursery		(15)	81.2	(15)	81.2		
	Others under 17		(43)	18.8	(13)	59.6	(30)	11.4
	Preschool	Urine µg/l	(5)	15.8			(5)	15.8
	Preschool + Nursery		(27)	14.5	(27)	14.5		
	Others under 17		(63)	10.3	(21)	13.0	(42)	9.1
	Preschool	Feces µg/g	(5)	0.92			(5)	0.92
	Preschool + Nursery		(17)	1.09	(17)	1.09		
	Others under 17		(58)	1.07	(20)	0.86	(38)	1.28
Years of Residence	0-1	Blood µg/100 ml	(34)	13.5	(29)	14.6	(5)	8.7
	2-3		(59)	12.0	(42)	13.3	(17)	9.2
	4+		(139)	11.2	(46)	15.1	(93)	9.7
	0-1	Long Hair µg/g	(33)	19.9	(28)	22.4	(5)	10.3
	2-3		(57)	22.3	(41)	27.4	(16)	13.2
	4 +		(123)	16.5	(39)	32.9	(84)	12.0

Factor	**Levels**	**Tissue**	(No. of Participants), Geometric Lead Mean					
			Total Baseline		Los Angeles		Lancaster	
Years of Residence	0-1	Short Hair µg/g	(26)	21.3	(22)	24.9	(4)	8.9
	2-3		(47)	28.4	(35)	35.0	(12)	15.4
	4+		(97)	16.4	(29)	37.5	(68)	11.5
	0-1	Urine µg/l	(34)	9.5	(29)	9.1	(5)	12.3
	2-3		(68)	10.0	(50)	10.8	(18)	8.1
	4 +		(141)	9.6	(47)	13.5	(94)	8.1
	0-1	Feces µg/g	(35)	0.64	(30)	0.63	(5)	0.70
	2-3		(61)	0.82	(42)	0.69	(19)	1.19
	4 +		(129)	0.84	(43)	0.70	(86)	0.92
Distance from Expressway	< 2 blks	Blood µg/100 ml	(97)	14.9	(95)	15.1	(2)	6.9
	2 blks - 1 mile		(65)	11.3	(24)	14.3	(41)	9.8
	> 1 mile		(80)	9.6	(5)	10.2	(75)	9.6
	< 2 blks	Long Hair µg/g	(89)	27.4	(88)	28.4	(1)	2.7
	2 blks - 1 mile		(56)	17.7	(20)	32.0	(36)	12.7
	>1 mile		(76)	12.0	(5)	10.9	(71)	12.1
	< 2 blks	Short Hair µg/g	(80)	32.6	(79)	33.4	(1)	4.9
	2 blks - 1 mile		(37)	18.1	(11)	48.8	(26)	11.9
	>1 mile		(63)	12.1	(2)	26.5	(61)	11.8
	< 2 blks	Urine µg/l	(107)	11.7	(105)	11.7	(2)	9.8
	2 blks - 1 mile		(65)	9.3	(24)	11.9	(41)	8.0
	>1 mile		(82)	8.4	(5)	7.5	(77)	8.5
	< 2 blks	Feces µg/g	(96)	0.75	(94)	0.74	(2)	1.57
	2 blks - 1 mile		(62)	0.82	(23)	0.59	(39)	0.98
	>1 mile		(76)	0.89	(5)	0.47	(71)	0.93

Factor	Levels	Tissue	(No. of Participants), Geometric Lead Mean					
			Total Baseline		Los Angeles		Lancaster	
Distance from Highway	<2 blks	Blood	(133)	13.4	(107)	14.4	(26)	10.0
	2 blks - 1 mile	µg/100 ml	(49)	11.2	(12)	18.3	(37)	9.6
	>1 mile		(56)	9.6	(2)	14.8	(54)	9.4
	<2 blks	Long Hair	(124)	25.7	(101)	28.1	(23)	17.2
	2 blks - 1 mile	µg/g	(42)	13.5	(9)	27.2	(33)	11.2
	>1 mile		(52)	11.4	(1)	100.5	(51)	10.9
	<2 blks	Short Hair	(103)	28.6	(83)	30.8	(20)	21.2
	2 blks - 1 mile	µg/g	(29)	15.5	(6)	93.3	(23)	9.7
	>1 mile		(45)	11.0	(1)	310.1	(44)	10.2
	<2 blks	Urine	(143)	10.5	(117)	11.4	(26)	8.1
	2 blks - 1 mile	µg/l	(49)	9.4	(12)	12.4	(37)	8.6
	>1 mile		(58)	8.6	(2)	25.6	(56)	8.3
	<2 blks	Feces	(132)	0.81	(107)	0.71	(25)	1.39
	2 blks - 1 mile	µg/g	(47)	0.82	(11)	0.57	(36)	0.92
	>1 mile		(51)	0.82	(1)	0.77	(50)	0.82
Air Conditioning	None	Blood	(135)	13.5	(105)	15.0	(30)	9.1
	Window	µg/100 ml	(37)	10.2	(15)	11.5	(22)	9.5
	Central		(71)	10.1	(4)	15.1	(67)	9.9
	None	Long Hair	(126)	22.7	(97)	28.6	(29)	10.4
	Window	µg/g	(35)	14.7	(14)	19.4	(21)	12.2
	Central		(61)	12.9	(2)	19.4	(59)	12.7
	None	Short Hair	(106)	29.1	(81)	36.1	(25)	14.5
	Window	µg/g	(27)	11.1	(10)	14.5	(17)	9.5
	Central		(49)	12.5	(3)	60.2	(46)	11.2

Factor	Levels	Tissue	(No. of Participants), Geometric Lead Mean					
			Total Baseline		Los Angeles		Lancaster	
Air Conditioning	None	Urine	(146)	10.6	(114)	11.5	(32)	8.0
	Window	µg/l	(38)	9.0	(16)	10.4	(22)	8.1
	Central		(71)	8.8	(4)	16.2	(67)	8.5
	None	Feces	(133)	0.78	(103)	0.71	(30)	1.08
	Window	µg/g	(38)	0.78	(16)	0.62	(22)	0.93
	Central		(64)	0.88	(3)	0.61	(61)	0.90
Cigarette Smoking	None	Blood	(172)	12.3	(90)	15.4	(82)	9.5
	<1/2 pack	µg/100 ml	(28)	11.3	(16)	12.7	(12)	9.7
	1/2 pack		(10)	9.7	(7)	10.6	(3)	8.0
	1 pack		(24)	11.7	(12)	14.7	(12)	9.2
	>1 pack		(8)	11.2	(0)		(8)	11.2
	None	Long Hair	(159)	21.6	(83)	32.9	(76)	13.6
	<1/2 pack	µg/g	(23)	14.3	(13)	18.4	(10)	10.3
	1/2 pack		(10)	13.5	(7)	12.6	(3)	15.9
	1 pack		(22)	8.9	(10)	1[illegible].0	(12)	5.5
	>1 pack		(7)	14.8	(0)		(7)	14.8
	None	Short Hair	(127)	22.8	(69)	40.7	(58)	11.5
	<1/2 pack	µg/g	(22)	14.9	(12)	16.5	(10)	13.2
	1/2 pack		(10)	17.6	(6)	14.7	(4)	23.1
	1 pack		(16)	16.2	(7)	31.7	(9)	9.6
	>1 pack		(6)	12.8	(0)		(6)	12.8
	None	Urine	(183)	10.5	(99)	12.4	(84)	8.7
	<1/2 pack	µg/l	(28)	7.1	(16)	8.3	(12)	5.8
	1/2 pack		(10)	10.8	(7)	12.4	(3)	7.7
	1 pack		(24)	7.6	(12)	8.7	(12)	6.5
	>1 pack		(8)	12.1	(0)		(8)	12.1

Factor	Levels	Tissue	(No. of Participants), Geometric Lead Mean					
			Total Baseline		Los Angeles		Lancaster	
Cigarette Smoking	None	Feces	(163)	0.85	(87)	0.74	(76)	0.99
	<1/2 pack	µg/g	(29)	0.81	(16)	0.68	(13)	1.02
	1/2 pack		(10)	0.74	(7)	0.53	(3)	1.58
	1 pack		(24)	0.64	(12)	0.53	(12)	0.77
	>1 pack		(7)	0.64	(0)		(7)	0.64
Ethnic Group	Mexican	Blood	(1)	12.1	(1)	12.1	(0)	
	Black	µg/100 ml	(19)	12.3	(16)	13.1	(3)	8.6
	Oriental		(5)	11.8	(1)	12.1	(4)	11.7
	White		(87)	10.3	(28)	12.4	(59)	9.5
	Mexican	Long Hair	(1)	3.7	(1)	3.7	(0)	
	Black	µg/g	(18)	29.5	(15)	33.4	(3)	15.8
	Oriental		(5)	18.3	(1)	86.7	(4)	12.4
	White		(82)	13.8	(28)	17.6	(54)	12.1
	Mexican	Short Hair	(1)	8.8	(1)	8.8	(0)	
	Black	µg/g	(7)	29.4	(3)	95.2	(4)	12.2
	Oriental		(4)	5.4	(1)	3.8	(3)	6.1
	White		(64)	16.5	(22)	28.6	(42)	12.4
	Mexican	Urine	(2)	5.2	(1)	5.7	(1)	4.7
	Black	µg/l	(19)	9.9	(16)	10.7	(3)	6.8
	Oriental		(5)	10.9	(1)	7.7	(4)	11.9
	White		(90)	9.3	(30)	11.8	(60)	8.2
	Mexican	Feces	(1)	0.39	(1)	0.39	(0)	
	Black	µg/g	(19)	0.66	(16)	0.66	(3)	0.66
	Oriental		(5)	1.30	(1)	0.39	(4)	1.76
	White		(80)	0.78	(26)	0.55	(54)	0.93

Factor	Levels	Tissue	(No. of Participants), Geometric Lead Mean Total Baseline		Los Angeles		Lancaster	
Occupation	Full time employment Part time employment	Blood µg/100 ml	(77) (24)	10.4 12.9	(30) (15)	12.6 14.4	(47) (9)	9.3 10.6
	Full time employment Part time employment	Long Hair µg/g	(70) (21)	11.2 17.6	(26) (12)	13.0 24.0	(44) (9)	10.2 11.7
	Full time employment Part time employment	Short Hair µg/g	(58) (17)	14.3 23.3	(23) (9)	19.7 34.3	(35) (8)	11.8 15.0
	Full time employment Part time employment	Urine µg/l	(78) (24)	8.1 9.6	(30) (15)	9.2 12.0	(48) (9)	7.6 6.7
	Full time employment Part time employment	Feces µg/g	(73) (24)	0.69 0.77	(29) (15)	0.53 0.58	(44) (9)	0.83 1.23